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THE SOLVOLYSIS AND REARRANGEMENT OF
2-ARYL-2-PROPYL ARENESULFINATES

BY

ROBERT MERMELSTEIN

A THESIS

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled, "The Solvolysis and Rearrangement of 2-Aryl-2-propyl Arenesulfinates", submitted by Robert Mermelstein in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The reaction of a number of 2-aryl-2-propyl 2,6-dimethylbenzenesulfonates in a variety of hydroxylic solvents was examined. The principal reaction appears to be that of solvolysis, accompanied by a variable degree of rearrangement to the corresponding sulfones. In ethanol, the rate of reaction of 2-p-nitrophenyl-2-propyl, 2-p-bromophenyl-2-propyl, 2-phenyl-2-propyl, 2-p-tolyl-2-propyl and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfonates are of the relative order expected for an ionization reaction. Solvolysis and rearrangement are almost equally sensitive to changes in the ionizing power of the solvent. These results are consistent with an ionic mechanism.

For both 2-phenyl-2-propyl and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfonates no common ion rate depression is observed during solvolysis, and the yield of sulfone is unaffected by the presence of added 2,6-dimethylbenzenesulfonate ion. Under comparable conditions, the reaction of the corresponding bromides in the presence of 2,6-dimethylbenzenesulfonate ion gives rise to negligibly small amounts of sulfone. The reaction of the esters in the presence of tetrabutylammonium 4-methylbenzenesulfonate does not yield any of the exchanged sulfone. These results are consistent with an ionic intramolecular rearrangement for sulfone formation. Ion pair return has thus been detected by the sulfonate-sulfone rearrangement.

Examination of the kinetic data and product analyses from the reaction of 2-p-bromophenyl-2-propyl and 2-p-tolyl-2-propyl

2,6-dimethylbenzenesulfonates in ethanol disclosed that these arene-sulfonate esters as well underwent reaction exclusively with carbon-oxygen bond cleavage. In contrast, the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfonate in ethanol takes place by both carbon-oxygen and sulfur-oxygen bond cleavage.

An examination of the effect of azide ion on the reaction of the 2-phenyl-2-propyl system provides unequivocal evidence that at least two species are precursors for solvolysis products, and at least one of them is an ion pair. Sulfone cannot be trapped effectively by azide ion. In the reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfonate, azide ion serves as an effective trapping agent for the precursors of both solvolysis product and sulfone. The results require at least one common intermediate, which is an ion pair and in principle, can be completely diverted to give the corresponding azide.

A correlation between the rates observed and the $\rho\sigma^+$ relationship has been made. A comparison of sulfone formation from various arenesulfonate esters is given.

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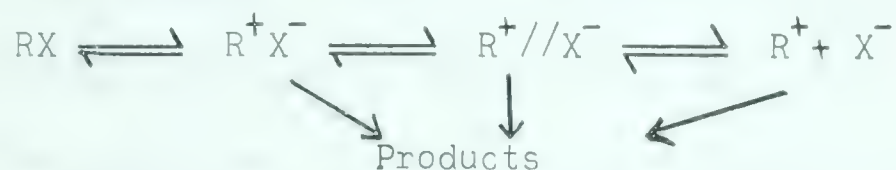
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INTRODUCTION

The study of solvolysis reactions through the past thirty years has become one of the most fruitful areas of research in the field of physical-organic chemistry. Many solvolysis reactions have been shown to involve ionization of the substrate, resulting often in products of partially inverted configuration (1). Racemic solvolysis products would be expected to be formed if free carbonium ions were the only intermediates involved. The intervention of ion pairs in solvolysis to explain the partially inverted configuration of α -phenylethyl acetate formed in the acetolysis of the bromide was first suggested by Hammett (2). Experimental evidence of the importance of ion pairs was first reported by Young, Winstein and Goering (3) who studied the acetolysis of α,α -dimethylallyl chloride. Solvolysis of this compound is accompanied by rearrangement to γ,γ -dimethylallyl chloride. The first-order rate constants drifted rapidly downward from the initial values. The final value of the observed first-order rate constant was the same as that for γ,γ -dimethylallyl chloride. When solvolysis of the initially pure α,α -dimethylallyl chloride was stopped after 35 per cent reaction, only γ,γ -dimethylallyl chloride was isolated. Addition of chloride ion had no effect on the rate. Common ion rate depression would be expected if the rearrangement involved free allylic carbonium ions. These results can be best explained by a concurrent intramolecular rearrangement and solvolysis involving a common intermediate. This intermediate ion pair can partition itself in a number of ways: return to

starting material or rearranged chloride, or react with solvent to form the respective acetates.

In the past decade, considerable further evidence has been presented on the importance of ion pairs in solvolysis. Extensive study of the solvolysis of various compounds led Winstein and co-workers (4) to propose a scheme which involves two types of ion pairs:



R^+X^- is an "intimate ion pair" in which the two ions are held in close proximity such that no solvent molecules are between them. $\text{R}^+//\text{X}^-$ is the "external or solvent separated ion pair" in which the oppositely charged ions are separated by a small number of solvent molecules, but held together as one unit in the solvent. Products may be formed from both ion pairs, as well as from free ions.

In the acetolysis of threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25°, the polarimetric rate constant exceeds the titrimetric rate constant by a factor of four (5). Added p-bromobenzenesulfonate ion has no effect on the rate of the reaction. Addition of lithium perchlorate gives rise to a linear increase in the polarimetric rate, which is usually referred to as a "normal salt effect." In contrast, the titrimetric rate under the same conditions shows a steep rise up to ca. .03 M lithium perchlorate concentration (special salt effect) followed by a linear increase. When the linear portion of the curve is extrapolated to zero lithium perchlorate concentration, the k_0 intercept (ext.) is about 2.6 times the observed titrimetric rate in the absence of lithium perchlorate. At no salt concentration is the titrimetric rate constant

equal to the polarimetric rate constant. These results are illustrated in Figure I. Ionization of the starting material would be expected to yield the symmetrically bridged ion, hence the loss of optical activity is measured by the polarimetric rate. Since the steep rise in rate on addition of lithium perchlorate affects only the titrimetric rate and not the polarimetric rate, it cannot be an ionic strength phenomenon on the ionization rate and must be concerned with the dissociation of ion pairs once they are formed. Lithium perchlorate prevents a fraction of ion pair return by exchanging with the ion pair produced to form the highly reactive carbonium perchlorate ion pair, which cannot return but solvolyzes rapidly. If all of the return were stopped, the polarimetric and titrimetric rate constants would be equal. This, however, has not been observed. The absence of common ion rate depression indicates that dissociated ions are not involved in the reaction. Therefore two types of ion pairs must be present, one of which is unaffected by the presence of lithium perchlorate.

If the acetolysis is carried out in the presence of lithium perchlorate and added common ion salt, lithium p-bromobenzene-sulfonate the observed titrimetric rate is considerably lower than that found in the presence of lithium perchlorate alone (6). Since the exchange reaction between the original ion pair formed and lithium perchlorate is reversible, the addition of the common ion salt should depress the special salt enhanced rate and thus give rise to "induced common ion rate depression," as illustrated below. The occurrence of such an induced depression in rate is further support for the exchange mechanism of the "special salt effect."

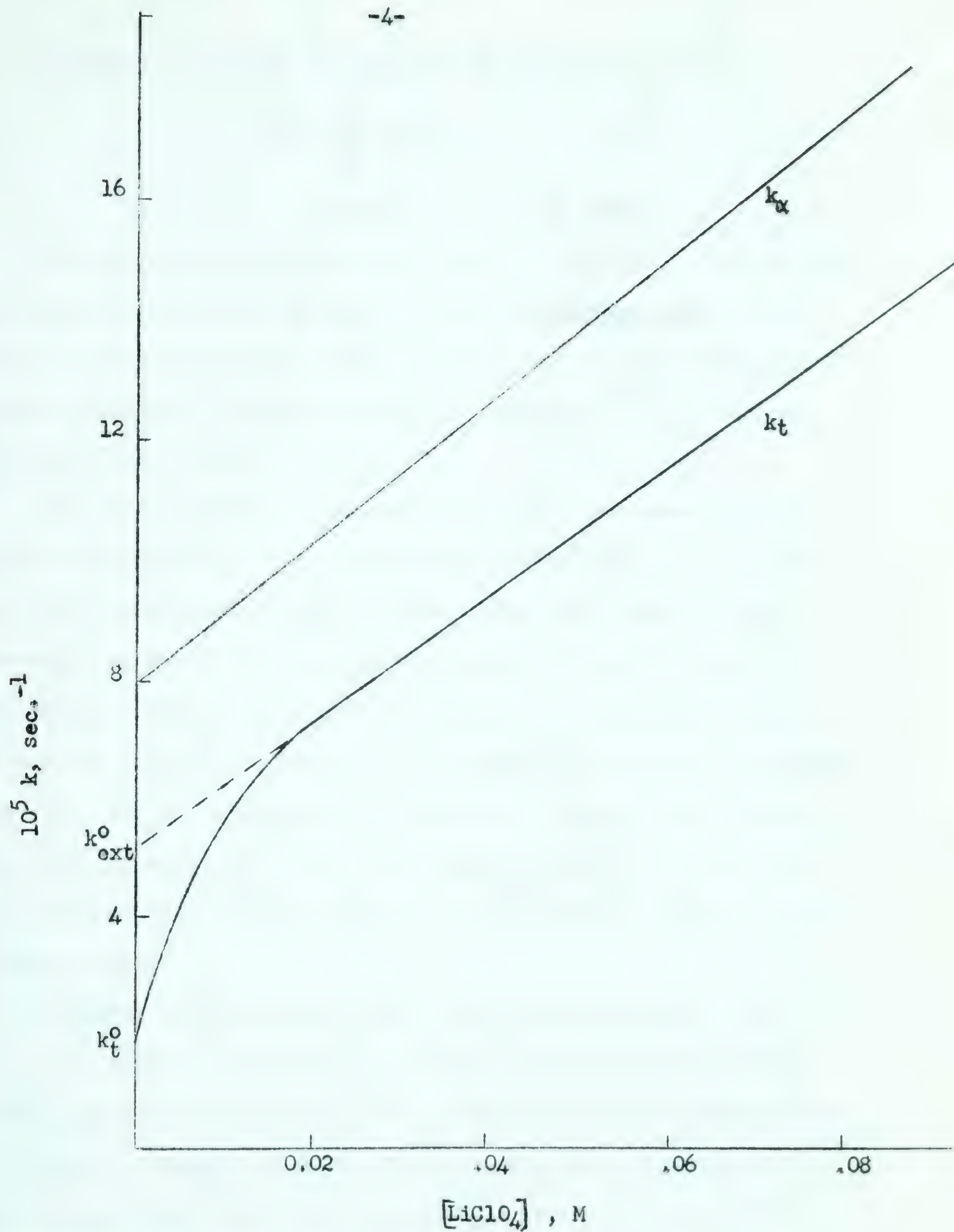
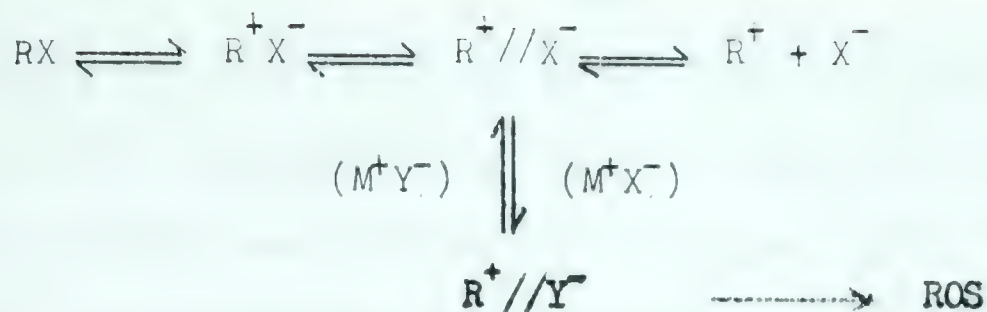


FIGURE I

Effect of lithium perchlorate on acetolysis of threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25° (taken from S. Winstein & G.C. Robinson, J. Am. Chem. Soc., 80, 169 (1958).)



Ion pair return has been also shown to take place in the solvolysis of optically active α, γ -dimethylallyl p-nitrobenzoate in 90% aqueous acetone and in other allylic systems (7). In the reaction of the above compound, the polarimetric rate constant is five times the titrimetric rate constant.

The previously described work demonstrated the presence of ion pairs in the solvolysis of compounds which yield symmetrically bridged ions and in symmetrical allylic systems. Here the ionization rate is reasonably assumed to be given by the racemization rate. In an open chain system, however, the intimate ion pair, $\text{R}^+ \text{X}^-$, may not be racemic and thus the ionization rate is not necessarily given by the polarimetric rate. The rate of racemization is a minimum estimate of the ionization rate, since ion pair return may take place without racemization. Hence one must resort to other means to try and detect ionization rates in these systems.

A number of methods have been used to detect ion pair return in open chain systems. In the case of substituted benzhydryl chlorides a method involving racemization of the carbonium ion has provided evidence for ion pairs. Racemization of optically active p-chlorobenzhydryl chloride was faster than its solvolysis by a factor of 2.5 in 80% acetone, and by a factor of 30-70 in acetic acid (8). In 80% acetone, the racemization rate was greater than the sum of the titrimetric rate

THE HISTORY OF THE CITY OF BOSTON

FROM THE
FIRST SETTLEMENT
TO THE PRESENT TIME

BY
JOSEPH NEALE

VOLUME I. FROM THE FIRST SETTLEMENT TO THE YEAR 1700.

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and exchange rate (with ^{36}Cl) by a factor of two. Since the exchange reaction gives the possible magnitude of common ion rate depression, racemization must take place without the formation of free ions and thus must involve ion pair return. Similar conclusions were arrived at by Pocker (9), who studied the solvolysis of optically active $\text{C}_6\text{H}_5\text{CDClC}_6\text{D}_5$ and $\text{C}_6\text{H}_5\text{CHClC}_6\text{D}_5$ in 80% acetone at 25° .

An alternate method used to detect ion pair return involves isotopic labelling of a portion of the leaving group. Exchange of ^{18}O between carbonyl and ether oxygens is three times faster than solvolysis in the reaction of benzhydryl *p*-nitrobenzoate carbonyl- ^{18}O in 90% aqueous acetone (10). The intramolecular oxygen equilibration accompanying solvolysis involves ion pair return.

Recently, Goering and coworkers (11) have presented additional evidence for the existence of two types of ion pairs. In the solvolysis of optically active *p*-chlorobenzhydryl *p*-nitrobenzoate carbonyl- ^{18}O in 80 and 90% aqueous dioxane, scrambling of the carboxyl oxygen atoms and racemization takes place. With added sodium azide, racemization is completely eliminated, while scrambling of the ^{18}O label still takes place (12). Goering states that two types of ion pairs must be present, as return from one gives racemization and scrambling, while return from the other results in scrambling only.

Recently, ion pair return has been detected in systems, where the anionic portion of the molecule can recombine with the carbonium ion to yield a stable product which is isomeric with the starting material. In solvolysis of benzhydryl thionbenzoate in ethanol, 83% thiolbenzoate and 17% benzhydryl ethyl ether is formed (13). Under identical

conditions the relative rates of reaction of *p*-methylbenzhydryl thionbenzoate and *p*-chlorobenzhydryl thionbenzoate compared to benzhydryl thionbenzoate are 17 and 0.53 respectively. Therefore the reaction is sensitive to substituent effects. When equimolar concentrations of potassium *p*-methoxythiobenzoate and benzhydryl thionbenzoate are allowed to react in ethanol, no benzhydryl *p*-methoxythiolbenzoate was formed. The absence of exchange indicates that dissociated ions are unimportant for the formation of rearranged products. Therefore, at least 83 per cent of the reaction proceeds by ion pairs. Similarly benzhydryl thiocyanate in a number of solvents yields predominantly benzhydryl isothiocyanate principally by ion pair return (14).

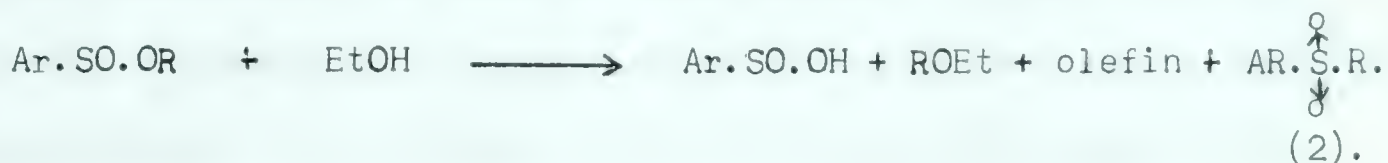
In the solvolysis of optically active arenesulfinate esters, racemization may take place on ion pair return in a manner similar to that observed with chlorides. In addition, ion pair return in arene-sulfinate esters may be accompanied by the formation of a new compound, a sulfone, isomeric with the starting material. Sulfones are stable under the expected reaction conditions (15).

In the solvolysis of carboxylate esters, alkyl or acyl-oxygen bond cleavage may take place. In an analogous manner, the solvolysis of arenesulfinate esters may proceed by sulfur-oxygen or carbon-oxygen bond fission. The extent to which each of the above processes will take place, depends on the structure of the ester and the reaction conditions used.

Ethanolysis of an arenesulfinate ester when sulfur-oxygen bond cleavage takes place, would be expected to yield the parent alcohol and ethyl arenesulfinate, as shown in equation 1.



If carbon-oxygen bond cleavage takes place under identical conditions, the expected products would include the sulfone, ethyl ether from the initial ester, olefin and sulfinic acid (provided no esterification of the latter takes place), as shown in equation (2).



Noreyko (16) has recently presented a discussion of sulfur-oxygen bond cleavage in similar systems. Since our interest lay primarily in the ionization reactions of arenesulfinate esters, only those systems which may involve carbon-oxygen bond cleavage will be mentioned in this section.

Kenyon and Phillips (17) noted that optically active α -phenylethyl 4-methylbenzenesulfinate on standing at room temperature yielded among other products racemic α -phenylethyl 4-methylphenyl sulfone. Solvolysis of the above ester in acetic acid resulted in the formation of racemic α -phenylethyl acetate and a little racemic α -phenylethyl 4-methylphenyl sulfone (18). Ethanolysis of the optically active ester yielded the corresponding ethyl ether of slightly inverted configuration. In contrast, solvolysis in ethanol in the presence of added potassium carbonate resulted in α -phenylethyl alcohol of completely retained configuration. The formation of α -phenylethyl alcohol of retained configuration indicates that sulfur-oxygen rather than carbon-oxygen bond cleavage was taking place. Racemic α -phenylethyl acetate and α -phenylethyl 4-methylphenyl sulfone must have been formed through carbon-oxygen bond cleavage. Similarly α -phenylethyl ethyl ether of

inverted configuration was formed by carbon-oxygen bond fission.

Solvolysis of optically active 4-methylbenzenesulfinate of ethyl 3-hydroxy-3-phenylpropionate in ethanol, resulted in the corresponding ethyl ether of partially inverted configuration (19). In the presence of potassium carbonate, the above ester in ethanol yielded principally the alcohol of completely retained configuration. These results suggest that carbon-oxygen bond cleavage was taking place in the absence of potassium carbonate. The formation of ethyl 3-hydroxy-3-phenylpropionate from ethanolysis in the presence of potassium carbonate is indicative of sulfur-oxygen bond cleavage. Similarly acetate and formate of retained configuration were the products of acetolysis and formolysis, once again suggesting sulfur-oxygen bond cleavage to be the principal reaction.

In a later publication the solvolysis of optically active α -phenylethyl 4-methylbenzenesulfinate was re-examined (20). In formic acid a 60 per cent yield of racemic sulfone was isolated after purification. Solvolysis of the ester, (1 molar) in formic acid containing sodium formate (2.5 molar), resulted in the isolation of only 10 per cent sulfone (purified). However, the sulfone was formed with 63 per cent net retention of configuration. The α -phenylethyl formate isolated in the above reaction was also of partially retained configuration, indicating that sulfur-oxygen bond cleavage was also taking place. Kenyon suggested that sulfone formation occurred by two paths, racemic sulfone was formed by ionization, while sulfone of retained configuration arose via a non-ionic intramolecular rearrangement. Streitwieser proposed (21) that sulfone of retained configuration may be formed by

ion pair return.

Cope, Morrison and Field (22) studied the thermal rearrangement of allylic benzenesulfinates. Both α -methylallyl and γ -methylallyl benzenesulfinate in toluene at 100° gave rise to about 20% γ -methylallyl-phenyl sulfone. The authors suggested that sulfone formation may occur by any of the following three paths, but could not make a definite decision among them: allylic rearrangement to yield sulfone, followed by the formation of a mixture of the two possible sulfones, or allylic rearrangement to give a mixture of the two sulfinic acid esters, followed by rearrangement to yield sulfone; or by an ionic mechanism.

Wragg, McFadyen and Stevens (23) investigated the rearrangement of a number of arenesulfinic acid esters in polar and non-polar media. They found that benzhydryl 4-methylbenzenesulfinic acid rearranged to the corresponding sulfone in acetic acid and in nitromethane, but in acetonitrile, benzene or toluene, no reaction took place unless 4-methylbenzenesulfinic acid was added. When the reaction in acetic acid was carried out in the presence of *p*-chlorobenzenesulfinic acid, benzhydryl *p*-chlorophenyl sulfone was also detected. Qualitatively, the rates of rearrangement of the homogeneous 4-methylbenzenesulfinates, were found to be in the order cumyl $> \alpha$ -phenylethyl ; *o*-methylbenzhydryl $>$ benzhydryl. The above order is consistent with a rate determining ionization. The sulfone yields also followed the above order. However, acid catalysis may have taken place, as no base was added, nor were rate constants measured. The fact that exchange was observed in the formation of sulfone is also consistent with an ionization process.

Recently McLaren (24) has shown that the sulfone formed in the

solvolysis of α -phenylethyl 2,6-dimethylbenzenesulfinate in 60% ethanol is almost completely of retained configuration. Solvolysis of α -phenylethyl bromide in the presence of 2,6-dimethylbenzenesulfinic acid under the above conditions does not give rise to significant amounts of α -phenylethyl 2,6-dimethylphenyl sulfone. Because the yield of sulfone is unaffected by the addition of 2,6-dimethylbenzenesulfinate ion in solvolysis, these results strongly suggest that sulfone arises through ion pair return.

The reaction of trityl 2-methylbenzenesulfinate in acetonitrile yields trityl 2-methylphenyl sulfone (25). When the reaction is carried out in the presence of tetrabutylammonium azide, there is no change in the rate of reaction, however, a maximum of ca. 45 per cent trityl azide is formed. These results were interpreted in terms of two distinct intermediates, an intimate ion pair and either a solvent separated ion pair or free ions or both.

Brown and coworkers (26) studied the solvolysis of ortho, meta and para substituted 2-phenyl-2-propyl chlorides in aqueous acetone. From the rate constants for solvolysis, a plot of $\log k$ versus the σ constants was made which was not linear for the para substituted compounds. Principal deviations were caused by electron donating substituents whose rate constants were faster than predicted by the σ values. A new relationship $\rho\sigma^+$ was defined, causing all of the points to fall on a single straight line. The authors also suggested the use of σ^+ values rather than σ in describing strong resonance interactions of electron donating substituents with electron deficient centers. Brown and coworkers assumed that the ionization rate constants were given by

the measured solvolysis rate constants. Since their data gave no information at all on ion pair return, ionization rate constants may be very much higher than the observed solvolysis rate constants.

The study of tertiary arenesulfinate esters could give valuable information on ion pair return in these systems. 2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate is a tertiary arenesulfinate ester, in which substituent effects on the rate of reaction could also be studied. Therefore, an investigation of the reactions of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate and its para substituted derivatives was initiated.

CHAPTER I

THE IONIZATION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE

INTRODUCTION

In this chapter the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate and its ethanolysis products is described. Solvolysis of this arenesulfinate ester in the presence of weak bases was studied in a number of solvents including ethanol, aqueous ethanol, aqueous dioxane and acetic acid. The effect of added salts was evaluated. Most of the results were obtained in anhydrous ethanol and acetic acid. Results of product isolation in anhydrous and aqueous ethanol are also given.

RESULTS

Preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate

The reaction between acetophenone and methylmagnesium iodide in ether solution afforded 2-phenyl-2-propanol. During the isolation procedure care was taken to wash the ethereal solution thoroughly with water to remove any acidic impurities which may catalyze the elimination reaction to form 2-phenylpropene. The infrared spectrum (carbon disulfide) of the material showed absorption at 3580 and 3480 cm^{-1} , characteristic of alcohols. The n.m.r. spectrum (carbon disulfide) showed a complex multiplet at 3.0 τ and two singlets at 6.75 and 8.65 τ in the ratio of 5:1:6. The multiplet at low field is due to the five aromatic protons; the high field singlet is assigned to the six methyl protons, while the signal at 6.75 τ is due to the hydroxyl proton.

2,6-Dimethylbenzenesulfinic acid was prepared by treatment of 2,6-dimethylaniline with nitrous acid; the solution was saturated with sulfur dioxide, followed by the addition of copper powder. (27) Structural assignment was made on the basis of the n.m.r. spectra. Singlets at -5.65 and 7.18τ (pyridine) in the ratio of 1:6 are ascribed to the acidic and the six methyl protons, respectively; in methanol, signals at 2.85 and 7.35τ in the ratio of 1:2 are assigned to the three ring and six methyl protons, respectively. The infrared spectrum (nujol) showed a broad band around 2480 cm^{-1} and a sharp band at 1050 cm^{-1} among others. Bellamy (28) states that sulfinic acids in solution exhibit a strong band near 1090 cm^{-1} . The sulfinic acid thus obtained was sufficiently pure for preparative purposes; however, for use in kinetic runs it was recrystallized from wet ethanol. The neutralization equivalent of 170.4 compares well with the calculated value of 170.2.

Treatment of 2,6-dimethylbenzenesulfinic acid with thionyl chloride in pentane gave rise to 2,6-dimethylbenzenesulfinyl chloride. Due to its facile hydrolysis, the acid chloride was not characterized, but allowed to react with 2-phenyl-2-propanol in pyridine at Dry Ice-acetone temperature. The ester was isolated by extraction with ether, and recrystallized from ether-pentane or pentane. The infrared spectrum of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate (carbon disulfide) showed a strong band at 1130 cm^{-1} , which is characteristic of sulfinate esters (28). The n.m.r. spectrum (carbon disulfide) showed signals at 2.9 (m), 7.58 (s), 8.18 (s), and 8.35τ (s) in the ratio of 8:6:3:3. The multiplet at low field, equivalent to eight protons, is due to the eight aromatic protons, while the singlet at 7.58τ is due to the six

methyl protons attached to the aromatic ring. The two singlets at high field are those of the aliphatic methyl groups. This splitting of the signal of substituents on the carbon atom adjacent to the arenesulfinate group will be discussed later.

Preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone

Our projected synthetic route for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone involved the reaction of 2,6-dimethylthiophenol with either 2-phenyl-2-propanol or 2-phenylpropene according to method E of Ipatieff (29) to give the sulfide, which on oxidation with hydrogen peroxide would be expected to yield the sulfone.

2,6-Dimethylthiophenol was prepared by the method of Tarbell and Fukushima (30). Diazotization of 2,6-dimethylaniline with nitrous acid, followed by treatment with potassium ethyl xanthate, gave 2,6-dimethylphenyl ethyl xanthate which on alkaline hydrolysis afforded 2,6-dimethylthiophenol. The infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly donated by R. A. McLaren. Attempted preparation of the sulfide by the above method or variations of it did not succeed. Attempts to prepare the sulfone by either the method of Balfe and Kenyon(31) or that of Wragg, McFadyen and Stevens (23) proved equally unsuccessful. The former method involves the reaction of 2-phenyl-2-propanol with sodium 2,6-dimethylbenzenesulfinate in acetic acid at room temperature, while the latter procedure calls for the reaction of 2-phenyl-2-propanol with 2,6-dimethylbenzenesulfinic acid in acetic acid at 90° in the presence of hydrochloric acid. The reaction of 2-phenyl-2-propanol with 2,6-dimethylbenzenesulfinic acid in

formic acid containing sodium formate, according to the method of Davies, Forster and Nery (32), gave rise to good yields of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. The infrared spectrum (carbon tetrachloride) of this material showed strong absorption at 1308 and 1135 cm^{-1} , characteristic of sulfones (28). The n.m.r. spectrum (carbon disulfide) exhibited signals at 2.8 (m), 7.92 (s), 8.30 τ (s) in the ratio of 4:3:3. The multiplet at low field is due to the eight aromatic protons on the two aromatic rings, while the singlets at 7.92 and 8.30 τ are due to the six aromatic and six aliphatic methyl protons.

Preparation of Solvolysis Products

Dehydration of 2-phenyl-2-propanol with phosphoric acid gave rise to 2-phenylpropene. The infrared spectrum of the material (neat) showed strong absorption at 1625 and 895 cm^{-1} which is characteristic of unsaturated compounds (33). The n.m.r. spectrum (carbon tetrachloride) showed signals at 2.7 (m), 4.76 and 5.00 (m) and 8.05 τ (d) in the ratio of 5:2:3, which are assigned to the five aromatic, two olefinic and three methyl protons respectively.

Preparation of the expected ethanolysis product, 2-phenyl-2-propyl ethyl ether, was effected by reaction of 2-phenyl-2-propanol with anhydrous ethanol in the presence of concentrated sulfuric acid, according to the procedure of Wallis and Bowman (34). The n.m.r. spectrum (carbon tetrachloride) showed signals at 2.7 (m), 6.85 (q), 8.55 (s) and 8.90 τ (t) in the ratio of 5:2:6:3. The multiplet at low field, equivalent to five protons, is due to the five aromatic protons; the singlet at 8.55 τ to six methyl protons, while the quartet and

triplet in the ratio of 2:3 have been assigned to the ethyl grouping of the molecule.

Treatment of 2-phenylpropene with hydrogen bromide in methylene chloride solution gave rise to 2-phenyl-2-propyl bromide, following removal of solvent. Volhard titration gave a molecular weight of 203 which corresponds to 98 per cent purity, based on a calculated molecular weight of 199.1. The n.m.r. spectrum (carbon tetrachloride) showed a multiplet at 2.65τ and a singlet at 7.92τ in the ratio of 5:6. The signal at low field is due to the five aromatic protons, while the singlet is due to the six methyl protons.

When 2-phenyl-2-propyl bromide was allowed to react with sodium azide in aqueous acetone, a mixture of 2-phenyl-2-propyl azide, olefin and alcohol was obtained. 2-Phenyl-2-propyl azide was separated by chromatography on alumina and exhibited intense absorption at 2100 cm^{-1} . The n.m.r. spectrum (carbon tetrachloride) showed only two signals, a multiplet at 2.75τ and a singlet at 8.45τ in the ratio of 5:6. Absorbance at 2100 cm^{-1} is typical of azides (35), while the n.m.r. signals are assigned unambiguously to the five aromatic and six methyl protons.

Kinetic Procedure

Kinetic runs were carried out in sealed ampoules at $70.04 \pm .03$ and $90.00 \pm .03^\circ$, and in volumetric flasks at $0.00 \pm .08$ and $25.00 \pm .03^\circ$. The initial concentration of arenesulfinate ester was .020-.025 M with a few exceptions. For the reactions carried out at 70 and 90° , one ampoule which was not put into the constant temperature bath was reserved

as a "blank."

When the solvent used was ethanol, aqueous ethanol or aqueous dioxane, 2,6-lutidine was the added base. Lutidinium 2,6-dimethylbenzene-sulfinate formed in solvolysis was titrated with sodium methoxide to the pink end point of phenolphthalein. From the titers obtained, the first-order rate constant was calculated by means of the equation,

$$k = \frac{2.303}{t} \log \frac{(T_{\infty} - T_0)}{(T_{\infty} - T)}$$

where T is the titer at time t.

The rate constants are based on experimental "infinity" values and thus measure the total rate of reaction. Generally the reactions were followed to 80-85 per cent complete reaction. Percentage infinity titers shown are obtained by subtracting the titer of the "blank" from the experimentally observed "infinity titer," and dividing by the theoretical "infinity titer."

The sulfone produced in the reaction was measured by infrared spectrophotometry. Each sample was carried through a standard extraction procedure using pentane, and the latter removed. A standard amount of carbon tetrachloride was added to each sample and the percentage transmittance recorded in the infrared near 1308 cm^{-1} . From the values obtained, the first-order rate constant was calculated by means of the equation,

$$k = \frac{2.303}{t} \log \frac{(D_{\infty} - D_0)}{(D_{\infty} - D)}$$

where D is the absorbance at time t.

From the absorbances of the samples after at least ten half-lives

for the reaction, the concentration, and thus the percentage sulfone formed in the reaction could be calculated. Thus, for practically all runs in ethanol and aqueous dioxane solutions, the rate of arenesulfinate ester disappearance was measured both by titrimetry and infrared spectrophotometry.

By subtracting the absorbance of the "blank" from that of the "infinity point," the concentration of sulfone could be determined from the Lambert-Beer plot. Dividing the concentration of sulfone by the concentration of starting ester resulted in the fraction or percentage sulfone values listed in the various tables.

In rate runs where either sodium azide or tetrabutylammonium azide has been added, the transmittance due to 2-phenyl-2-propyl azide was also recorded between 2200 and 2000 cm^{-1} , and from the values obtained the first-order rate constants were calculated.

To determine whether or not the Lambert-Beer law was obeyed, an accurately weighed amount of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone was dissolved in 98% ethanol and quantitative dilutions of the solution thus prepared were effected by use of an automatic pipette. Aliquots of these solutions were carried through the same standard extraction procedure as used in the kinetic runs. The percentage transmittance of the carbon tetrachloride solutions of the sulfone was measured between 1400 and 1250 cm^{-1} . From the transmittance recorded at 1308 cm^{-1} the absorbance was calculated and plotted against the concentration of the sulfone. The relationship between optical density and concentration for 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone is given in Table I and Figure II. A linear relationship is observed up to

.005 M sulfone concentration. In this way a simultaneous check could be made on the extraction procedure as well as adherence to the Lambert Beer law.

TABLE I

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR
2-PHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE AS MEASURED
IN CARBON TETRACHLORIDE AT 1308 cm.^{-1} .

Sulfone, Molar	$\frac{I_0}{I}$	$\log \frac{I_0}{I}$
.008783	12.195	1.0862
.007026	9.019	.95516
.005270	5.926	.77276
.004392	4.635	.66605
.003513	3.456	.53857
.001756	1.927	.28488
.000878	1.356	.13226

Reaction in Anhydrous Ethanol

A control run was carried out on the stability of 2,6-dimethylbenzenesulfinic acid in anhydrous ethanol at 90° in the presence of added 2,6-lutidine. From the results recorded in Tables XL and XLI it is apparent that the acid titer is constant within experimental error for at least 177 hours.

Reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol gave rise to good first-order kinetics. The rate

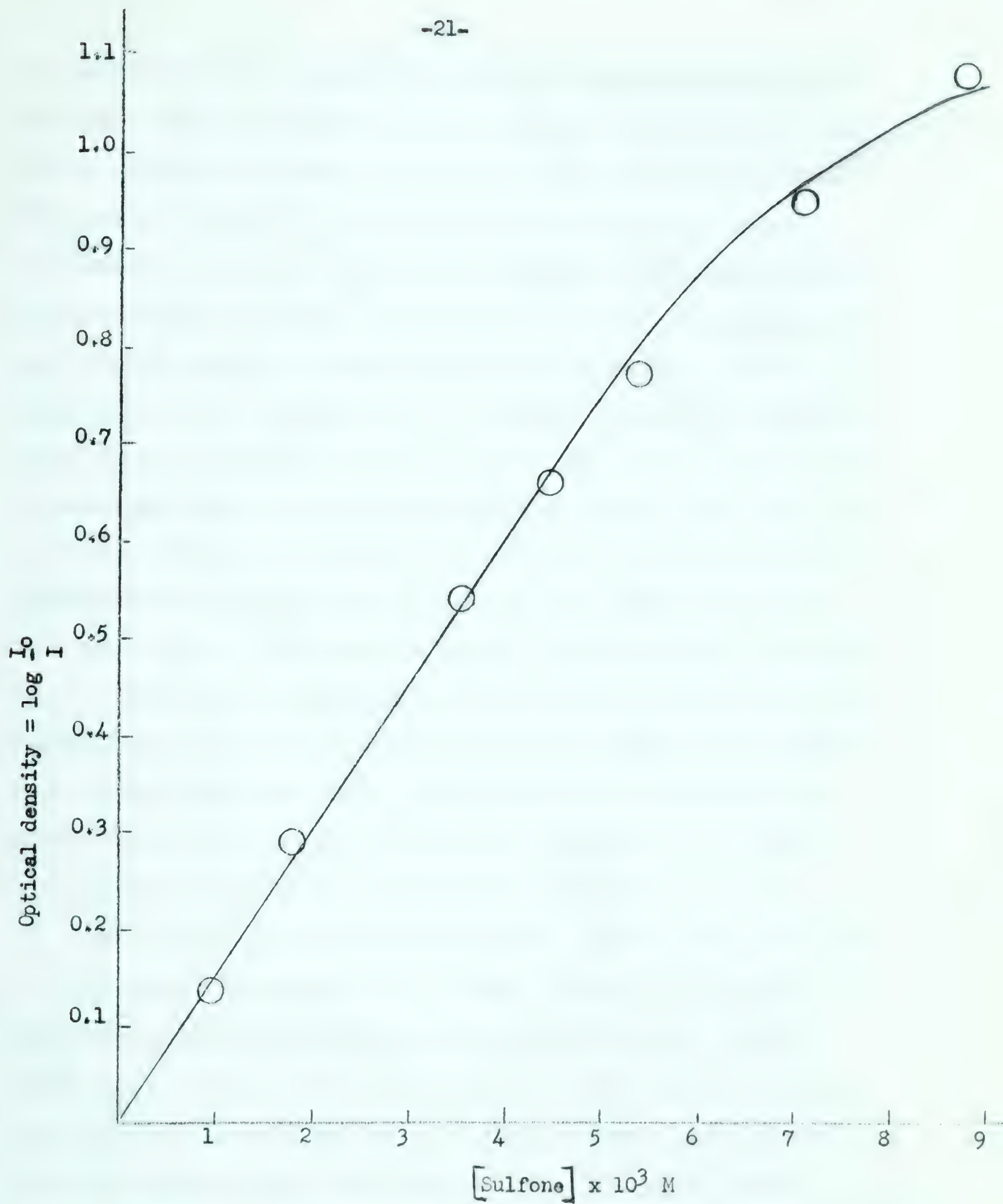


FIGURE II

The relationship between optical density and concentration for 2-Phenyl-2-propyl 2,6-dimethylphenyl sulfone in carbon tetrachloride at 1308 cm.⁻¹ ,

constants measured by titrimetry and infrared spectrophotometry are in most cases identical within experimental error, average deviations are 2.5 per cent with the former and less than 5 per cent with the latter. The principal reaction in ethanol appears to be that of solvolysis, accompanied by less than 10 per cent rearrangement to 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. The ratio of solvolysis to rearrangement is unaffected by changes in temperature as shown in Table II. Within experimental error, the same amount of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone is formed at 25, 70 and 90°. The rate of reaction at 90° is four times faster than at 70° and 1800 times faster than at 25°. In run II-171, Table XLII, carried out at 25°, the "infinity" values were obtained by immersing two ampoules into the 90° constant temperature bath for 10 hours. These ampoules had been previously kept in the 25° bath for 4056 hours, corresponding to more than three half-lives of the arenesulfinate ester at 25°. The ten hours in the 90° constant temperature bath are equivalent to ca. 12 half-lives of the arenesulfinate ester. Sample reaction rates, measured by titrimetry and infrared spectrophotometry are given in Tables XLIII and XLIV.

An increase in base concentration gives rise to a small decrease in the observed first-order rate constants. As shown in Table III, a change in the added 2,6-lutidine concentration from .044 to .129 M causes about a ten per cent decrease in rate. However, the extent of rate depression is small and may be within experimental error of the values recorded with ca. .05 M 2,6-lutidine. The change in base concentration has no significant effect on the amount of rearrangement. (Compare Runs II-69,70; I-125,126; and I-133,134.) The sharpness of the

end point in the titrations is considerably reduced in the presence of increased amounts of 2,6-lutidine.

TABLE II

SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ETHANOL AT VARIOUS TEMPERATURES WITH ADDED 2,6-LUTIDINE

Run No. ^a	Temp. ^o C	Ester 10 ² M	Base ^b 10 ² M	10 ⁴ k ₁ sec. ⁻¹	F _{solv.} ^c	F _{rear.} ^d
I-165	90 ^o	2.18	4.38	2.25 ± .04	.904	
I-166	90 ^o	2.18	4.38	2.20 ± .14		.099
I-292	70 ^o	2.23	4.62	.542 ± .012	.901	
I-293	70 ^o	2.23	4.62	.543 ± .014		.100
II-171	25 ^o	2.19	4.49	.00128 ± .00006	.905	
II-171	25 ^o	2.19	4.49	.00123 ± .00008		.102

^aThe "Run number" as used in this thesis is a laboratory notebook reference, e.g., I-165 refers to page 165 of the first laboratory notebook.

^b2,6-Lutidine.

^cFraction of reaction producing solvolysis products.

^dFraction of reaction producing rearrangement product, sulfone.

Addition of 2,6-dimethylbenzenesulfinate ion, (2,6-dimethylbenzenesulfinic acid and 2,6-lutidine) causes a small rate increase, but does not affect the amount of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone formed. (Compare Runs I-219,220; I-223,224 and I-165,166 in Table III.) There is no drift apparent in the first-order rate constants measured by either titrimetry or infrared spectrophotometry (Table XLIV, XLV).

The effect of added salts on the reaction was also studied, and the results are summarized in Table III. Addition of lithium perchlorate causes a linear increase in rate, as illustrated in Figure III (compare Runs I-185,186; I-129,130; I-161,162; I-181,182 and I-189,190 in Table III). The following equation has been suggested for the correlation of salt effects on rate constants:

$$k/k^0 = 1 + b[\text{salt}]$$

where k^0 is the observed rate constant in the absence of salt, k is the observed rate constant in the presence of salt and b is the percentage increase in rate per 1/100 M salt concentration (36). The "b" value for lithium perchlorate under the above conditions is $7.5 \pm .4$. As shown in Table III, the ratio of solvolysis to rearrangement product is unaffected by the addition of this salt. A sample rate in the presence of added lithium perchlorate is shown in Table XLVI.

Addition of tetrabutylammonium perchlorate gives rise to the same type of effects as lithium perchlorate but these effects are smaller in magnitude. Under these conditions, a "b" value of $1.0 \pm .1$ is obtained for tetrabutylammonium perchlorate. (See Runs II-58,59; II-63,64; II-73, 74, and II-79,80.) Sample rates are given in Table XLVII, while the results of the stability of 2,6-dimethylbenzenesulfinic acid in anhydrous ethanol at 90° in the presence of tetrabutylammonium perchlorate are recorded in Table XLVIII. The addition of tetrabutylammonium perchlorate has little if any effect on the stability of 2,6-dimethylbenzenesulfinic acid under the above conditions. The effect of perchlorate salts on the rate of reaction is summarized in Figure III.

TABLE III

SUMMARY ON SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ETHANOL AT 90.0°
WITH ADDED 2,6-LUTIDINE AND VARIOUS OTHER SALTS.

Run	Ester 10 ² M	2,6-Lutidine 10 ² M	Added Salt	Conc. 10 ² M	10 ⁴ k ₁ sec. ⁻¹	F solv.	F rear.
I- 72	2.49	4.65			2.25 ± .07	0.923	
I- 74	2.53	6.52			2.25 ± .13	.923	
II-69	2.20	4.38			2.22 ± .04*	.914	
II-70	2.20	4.38			2.20 ± .06		0.092
I-165	2.18	4.38			2.25 ± .04	.904	
I-166	2.18	4.38			2.20 ± .14		.099
I-125	1.85	12.86			2.01 ± .12	.890	
I-126	1.85	12.86			2.02 ± .06		.080
I-133	2.04	12.92			2.00 ± .03	.911	
I-134	2.04	12.92			1.86 ± .14		.089
I-223	2.20	9.34			2.12 ± .03	.913	
I-224	2.20	9.34			2.12 ± .13		.098
I-219	2.22	9.35	ArSOOH(a)	1.95	2.46 ± .02	.913	
I-220	2.22	9.35	ArSOOH	1.95	2.58 ± .09		.096
I-185	2.15	4.60	LiClO ₄	0.86	2.39 ± .03	.907	
I-186	2.15	4.60	LiClO ₄	.86	2.44 ± .10		.092
I-129	2.15	4.68	LiClO ₄	1.51	2.52 ± .09	.886	
I-130	2.15	4.68	LiClO ₄	1.51	2.50 ± .38		.100

continued

TABLE III continued.

Run	Es _{fer} 10 ⁻² M	2,6-Lutidine 10 ⁻² M	Added Salt	Conc. 10 ⁻² M	10 ⁴ k ₁ , sec.	F solv.	F rear.
I-161	2.15	4.56	LiClO ₄	1.56	2.64 ± .04		
I-162	2.15	4.56	LiClO ₄	1.56	2.53 ± .16		0.094
I-181	2.17	4.54	LiClO ₄	2.84	2.70 ± .04	0.908	
I-182	2.17	4.54	LiClO ₄	2.84	2.86 ± .21		.092
I-189	2.14	4.82	LiClO ₄	3.40	2.85 ± .05	.908	
I-190	2.14	4.82	LiClO ₄	3.40	2.81 ± .12		.095
II-58	2.17	4.48	Bu ₄ N ClO ₄	1.64	2.23 ± .08	.887	
II-59	2.17	4.48	Bu ₄ N ClO ₄	1.64	2.23 ± .12		.097
II-63	2.18	4.53	Bu ₄ N ClO ₄	3.04	2.35 ± .05	.898	
II-64	2.18	4.53	Bu ₄ N ClO ₄	3.04	2.29 ± .22		.096
II-73	2.23	4.67	Bu ₄ N ClO ₄	3.85	2.34 ± .02	.908	
II-74	2.23	4.67	Bu ₄ N ClO ₄	3.85	2.36 ± .09		.085
II-79	2.29	4.54	Bu ₄ N ClO ₄	8.74	2.45 ± .04	.908	
II-80	2.29	4.54	Bu ₄ N ClO ₄	8.74	2.38 ± .07		.088
II-100	2.23	4.50	Bu ₄ N Br	1.58	2.38 ± .09		.087
II-106	2.17	4.58	Bu ₄ N Br	3.41	2.31 ± .16		.092
II-112	2.17	4.51	Bu ₄ N Br	6.08	2.60 ± .12		.084
II-123	2.16	4.19	Bu ₄ N Br	3.34	2.29 ± .04	.885	
II-124	2.16	4.19	Bu ₄ N Br	3.34	2.46 ± .11		.085

continued

TABLE III continued.

Run	Ester 10 ² M	2,6-Lutidine 10 ² M	Added Salt	Conc. 10 ² M	10 ⁴ k ₁ sec. ⁻¹	F _{solv.}	Frear.	F _{azide}
II-143	2.14	4.42	Bu ₄ N Br	7.17	2.40 ± .05	0.905		
II-144	2.14	4.42	Bu ₄ N Br	7.17	2.46 ± .08		0.086	
II-120	2.18	4.40	KCNS	1.81	2.85 ± .13		.085	
II-128	2.16	4.42	KCNS	3.58	2.96 ± .10		.085	
II-218	2.20	4.26	Bu ₄ N SO ₂ C ₇ H ₇ (b)	19.96	2.43 ± .10	.903		
II-219	2.20	4.26	Bu ₄ N SO ₂ C ₇ H ₇	19.96	2.44 ± .08		.097	
II-179	2.18	4.44	Bu ₄ N N ₃	8.18	2.33 ± .06	.782		
II-180	2.18	4.44	Bu ₄ N N ₃	8.18	2.26 ± .14		.087	
II-181	2.18	4.44	Bu ₄ N N ₃	8.18	2.20 ± .23			0.122
II-191	2.19	4.68	Bu ₄ N N ₃	14.29	2.52 ± .03	.740		
II-192	2.19	4.68	Bu ₄ N N ₃	14.29	2.40 ± .07		.080	
II-193	2.19	4.68	Bu ₄ N N ₃	14.29	2.49 ± .14			.171
II-205	2.17	4.53	Bu ₄ N N ₃	29.09	2.55 ± .13	.679		
II-206	2.17	4.53	Bu ₄ N N ₃	29.09	2.46 ± .11		.073	.230
III-40(c)	2.26	4.52	Bu ₄ N N ₃	20.09	2.65 ± .03	.680	.083	.212
III-38(c)	2.23	4.24	Bu ₄ N N ₃	28.47	2.81 ± .06	.620	.071	.258

(a) 2,6-Dimethylbenzenesulfinic acid. (b) Tetra butylammonium 4-methylbenzenesulfinate

(c) Kinetic Method B used.

* When duplicate rate runs are listed, the first one is measured by titrimetry, the second one by infrared spectrophotometry.

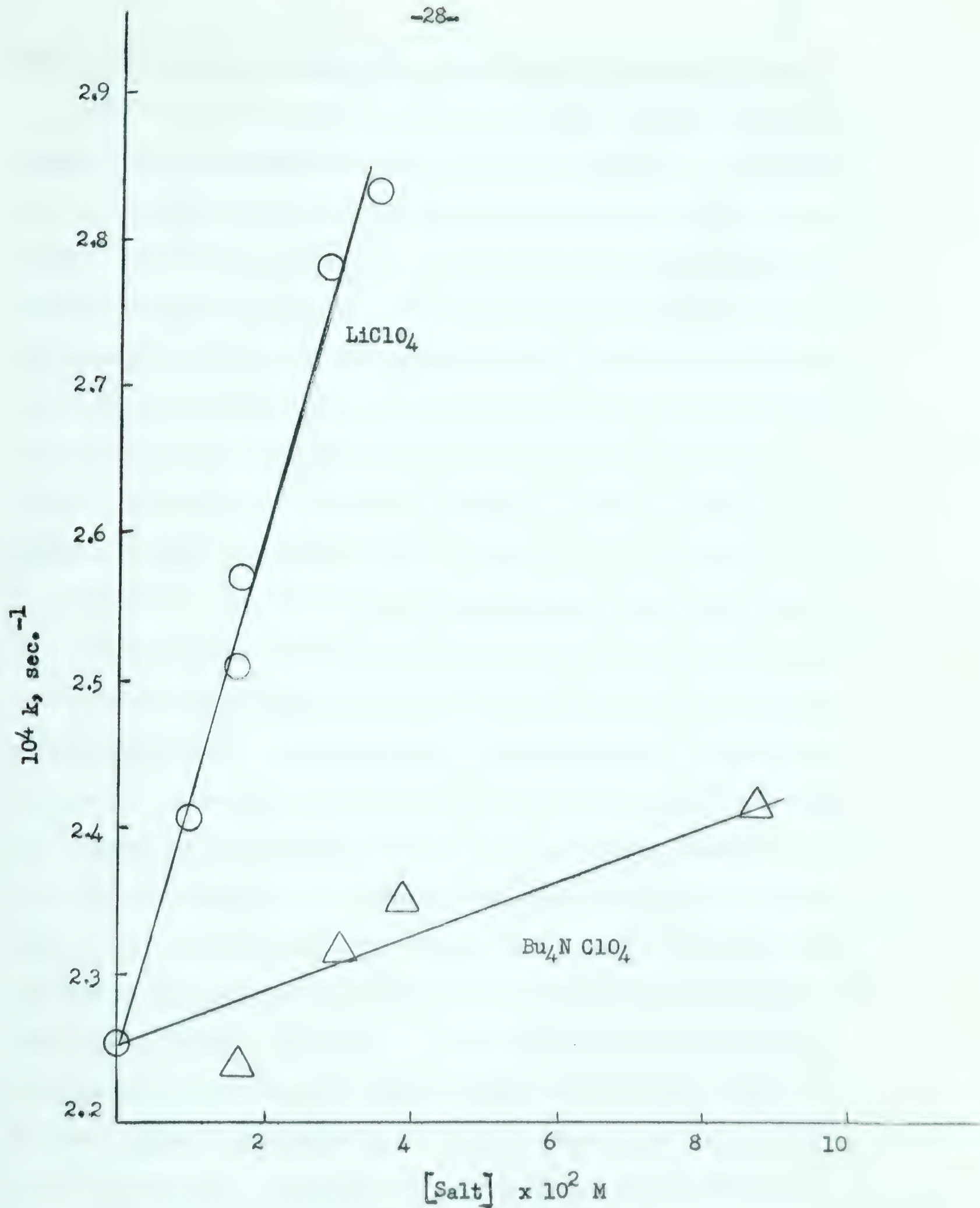


FIGURE III

The effect of perchlorate salts on reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° in the presence of 2,6-lutidine.

The Effect of Added Nucleophiles on Solvolysis in Anhydrous Ethanol

The effect of various nucleophiles on the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate was also examined. Uncorrected titrimetric rate constants in the presence of added tetrabutylammonium bromide tended to be less precise and considerably lower percentage infinity titers were obtained than in the absence of the salt. As shown in Tables XLIX, and L, the percentage infinity titers recorded seemed to depend on the concentration of the added bromide and the time at which the infinity titer was taken. Control runs on the stability of 2,6-dimethylbenzenesulfinic acid in anhydrous ethanol at 90° in the presence of added tetrabutylammonium bromide and 2,6-lutidine are given in Tables LI and LII and show the disappearance of acid titer with time.

Ethyl 2,6-dimethylbenzenesulfinate was isolated from the water insoluble portion of the above reaction mixture, and its concentration increased with time. Sample reaction rates measured by titrimetry are recorded in Tables XLIX and L, titers after one and a half half-lives are adjusted for the disappearance of 2,6-dimethylbenzenesulfinic acid. The corrections added to the observed titers are based upon the change in titer of ca. .02 M 2,6-dimethylbenzenesulfinic acid with time, in the presence of comparable concentrations of tetrabutylammonium bromide and 2,6-lutidine (Tables LI and LII). Sample reaction rates measured by infrared spectrophotometry are also recorded in Tables XLIX and L. The rate constants and percentage infinity values listed in Table III are corrected ones. It is apparent from Table III, that addition of tetrabutylammonium bromide has no effect on the ratio of solvolysis to rearrangement.

Addition of potassium thiocyanate resulted in erratic titers and lower percentage infinity titers than in the absence of the salt. A control (Table LIII) on the stability of 2,6-dimethylbenzenesulfinic acid in anhydrous ethanol at 90° in the presence of added 2,6-lutidine and potassium thiocyanate also showed erratic titers. Ethyl 2,6-dimethylbenzenesulfinate was isolated from the water insoluble portion of the above reaction mixture, and its concentration increased with time.

A sample rate of ester disappearance measured by infrared spectrophotometry is given in Table LIV. No absorption due to either 2-phenyl-2-propyl thiocyanate or 2-phenyl-2-propyl isothiocyanate was detected in the infrared between 3000 and 2000 cm^{-1} . From runs II-120 and II-128 (Table III) it is apparent that the fraction of sulfone at infinity is still unchanged within experimental error.

A number of kinetic runs using 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol in the presence of tetrabutylammonium azide were carried out and are reported in Table III. Addition of tetrabutylammonium azide caused a change in product distribution as shown in Table III. On increasing the added azide concentration from 0 to .28 M, the percentage solvolysis is decreased from ca. 91% to 62%; the percentage rearrangement is decreased from 9.5% to 7.1% and the percentage of 2-phenyl-2-propyl azide formed is increased from zero to 25.8%. Due to the relatively small amount of rearrangement observed in the absence of added salt ($9.5 \pm 1.0\%$) and consequent large relative error, it is difficult to decide whether the decrease in the amounts of sulfone measured in the presence of tetrabutylammonium azide is real, or experimental error. There is no doubt, however, as to the lower

percentage infinity titers and the formation of 2-phenyl-2-propyl azide as measured in the infrared at 2100 cm.^{-1} . Sample reaction rates are given in Tables LV, LVI and LVII. Runs III-38 and III-40 were carried out using the kinetic procedure B, in which only the rate of acid production was followed. From the infrared spectrum, the concentration of azide and sulfone at infinity were calculated.

The relationship between optical density and concentration for 2-phenyl-2-propyl azide was tested exactly as for 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. The results obtained are listed in Table IV and Figure IV. It is apparent that a linear relationship is obeyed.

TABLE IV

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR 2-PHENYL-2-PROPYL AZIDE AS MEASURED IN CARBON TETRACHLORIDE AT 2100 CM.^{-1}

Azide, Molar	$\frac{I_0}{I}$	$\log \frac{I_0}{I}$
.01049	8.981	.95332
.00839	5.503	.74060
.00630	3.963	.59802
.00420	2.297	.35116
.00210	1.381	.14019

A small rate enhancement was observed in the reaction of the arenesulfinate ester in the presence of .2 M tetrabutylammonium 4-methylbenzenesulfinate (Run II-218,219, Table III). The sulfone

formed in the reaction was isolated by the same procedure as used in product analysis (see page 44) and its n.m.r. spectrum recorded at 60 Mc. and 100 Mc. The n.m.r. spectrum showed the presence of only 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. A series of control experiments were run using mixtures of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone and 2-phenyl-2-propyl 4-methylphenyl sulfone. From these experiments we estimate that ca. 5% of 2-phenyl-2-propyl 4-methylphenyl sulfone could be detected in the presence of 95% 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, by measurement of n.m.r. spectra at the concentrations observed in the product runs. Hence less than 5% of the exchanged sulfone is present.

Solvolysis of 2-phenyl-2-propyl bromide

Solvolysis of 2-phenyl-2-propyl bromide (.02969 M) in the presence of 2,6-dimethylbenzenesulfinic acid (.03085 M) in anhydrous ethanol containing 2,6-lutidine was carried out for one hour. The actual rate constant for this reaction has not been measured, but a number of estimates of the rate can be made. α -Phenylethyl bromide in anhydrous ethanol at 25° has a first-order rate constant of $6 \times 10^{-6} \text{ sec.}^{-1}$ (37). If we allow a factor of 10^3 for the effect of the additional methyl group (38), 2-phenyl-2-propyl bromide would be expected to have a first-order rate constant of ca. $6 \times 10^{-3} \text{ sec.}^{-1}$. 2-Phenyl-2-propyl chloride in 90% acetone-water shows a first-order rate constant of $1.2 \times 10^{-4} \text{ sec.}^{-1}$ at 25° (39), thus one would expect in anhydrous ethanol at the same temperature a rate constant in the vicinity of $2 \times 10^{-4} \text{ sec.}^{-1}$ (3), since the two solvents have a similar γ value. If the change from chloride to bromide increases the rate by a factor of 30 (40), a first-order rate constant of ca. $6 \times 10^{-3} \text{ sec.}^{-1}$ is expected for the solvolysis of 2-phenyl-2-propyl bromide in anhydrous ethanol at 25°. Thus both approximations give a

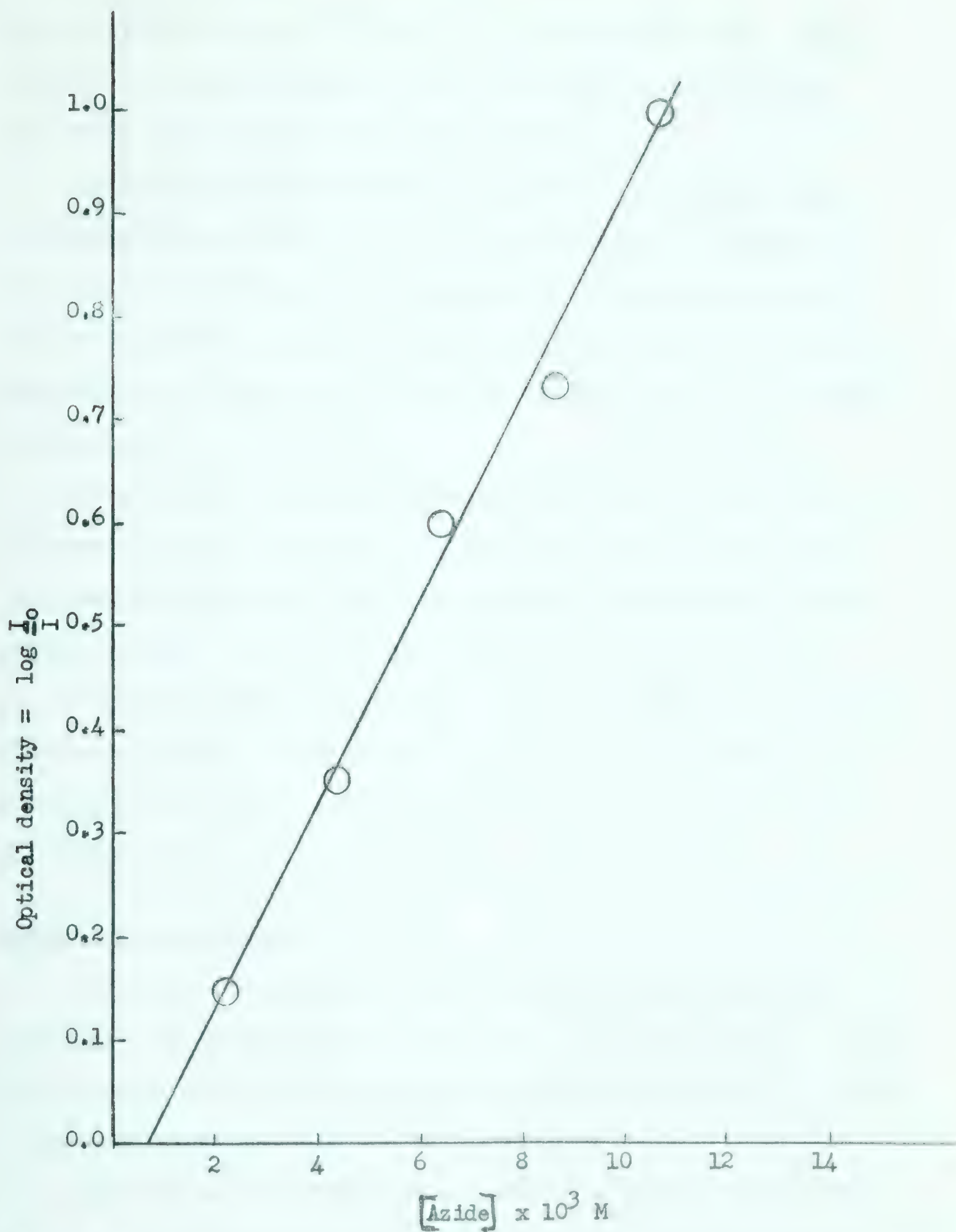


FIGURE IV

Relationship between optical density and concentration for 2-phenyl-2-propyl azide in carbon tetrachloride at 2100 cm.^{-1} .

rate constant of ca. $6 \times 10^{-3} \text{ sec.}^{-1}$ or a half-life of about three minutes. Therefore, a reaction time of one hour at 25° should be sufficient for the completion of the reaction.

The acid produced in the above reaction was titrated, and assuming a 95% purity for the starting 2-phenyl-2-propyl bromide and 100% purity for the starting 2,6-dimethylbenzenesulfinic acid, the theoretical amount of acid was formed. Volhard titration showed 95.4% bromide formed, justifying the assumption of 95% purity for the starting bromide.

Examination of the infrared spectrum (carbon tetrachloride) of the water insoluble material in the region of 1308 cm.^{-1} disclosed a very weak absorption which would correspond to 0.65% sulfone. However, 2-phenyl-2-propyl ethyl ether has a weak absorption band near 1305 cm.^{-1} , thus there may be considerably less than 0.65% 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone formed. Even if all of the absorbance measured is due to the sulfone, the amount would not exceed 7.5% of the sulfone formed in any of the kinetic runs.

Reaction in 80% Ethanol

Results on the stability of 2,6-dimethylbenzenesulfinic acid in 80% ethanol at 70° are given in Table LVIII. The acid titer is constant for 72 hours, which corresponds to about 100 half-lives for the reaction of the ester under our experimental conditions.

Reaction of the ester in 80% ethanol at 70° gave rise to 84% solvolysis and 16% rearrangement product. Sample rates are given in Table LIX. As shown in Table V, addition of 2,6-dimethylbenzenesulfinate ion has little if any effect on either the rate of reaction or the

amount of sulfone formed. There is no drift apparent in the reaction rates, measured by either titrimetry or infrared spectrophotometry (Table LX). The reaction at 90° in 80% ethanol is 5.8 times faster than the reaction at 70° under the same conditions. No change in ratio of solvolysis to rearrangement was discernible.

In Run I-299,300 shown in Table V, .1M sodium azide was added and ca. 9.5% 2-phenyl-2-propyl azide was formed. The percentage solvolysis value decreased from ca. 84% to 73%, while the value of the percentage sulfone formed changed from 16% to 14.1%. Due to the small change in sulfone measured in the presence and absence of added azide, it is difficult to decide whether significant reduction in the yield of sulfone took place, or **whether the values are, within experimental error, the same.**

A summary of the rates measured in 80% ethanol is given in Table V.

Reaction in Aqueous Dioxane

A number of rates were measured in 80 and 90% dioxane at 90° . As summarized in Tables LXI, LXII, LXIII, LXIV, aqueous dioxane heated at 90° generates acid. This reaction takes place in the presence and absence of 2,6-dimethylbenzenesulfinic acid. The amount of acid produced is reflected in the portion of the sum of $F_{\text{solv.}}$ plus $F_{\text{rear.}}$ exceeding unity as shown in Table VI. The development of acid by aqueous dioxane and aqueous acetone solutions at elevated temperatures has been noted by other workers (41,42). In 80% dioxane at 90° , the average sum of $F_{\text{solv.}}$ plus $F_{\text{rear.}}$ is 1.023 or 102.3%, while in 90% dioxane at 90° the amount is 1.056 or 105.6%. The rate constants listed in Table VI have



TABLE V

THE EFFECT OF ADDED SALTS ON THE SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENE-SULFINATE IN 80 % ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE.

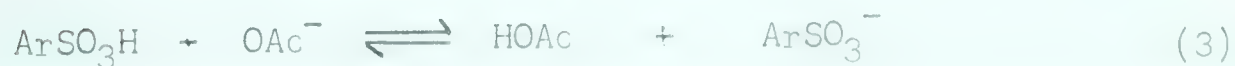
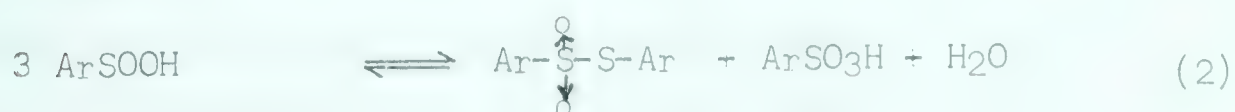
Run No.	Ester 10 ² M	Base ^(a) 10 ² M	Added Salt	Conc. 10 ² M	10 ⁴ k, sec. ⁻¹	F _{solv.}	F _{rear.}
I-78	1.67	4.09			3.52 ± .10	0.864	
I-82	1.81	4.48			3.63 ± .12	.849	
I-205 ^(b)	2.15	4.48			20.6 ± .3	.859	0.157
I-206	2.15	4.48			20.2 ± .5		
I-92	2.16	9.31			3.49 ± .06	.840	
I-103	2.15	9.23			3.65 ± .07	.810	.165
I-104	2.15	9.23			3.43 ± .14		
I-88	2.12	9.18	ArSOOH ^(c)	2.62	3.71 ± .17	.858	
I-99	2.15	9.14	ArSOOH	2.72	3.52 ± .07	.835	.165
I-100	2.15	9.14	ArSOOH	2.72	3.47 ± .27		
I-299 ^(d)	2.17	4.56	NaN ₃	10.0	7.10 ± .15	.734	.141
I-300	2.17	4.56	NaN ₃	10.0	7.45 ± .36		

(a) 2,6-Lutidine (b) at 90.0° (c) 2,6-Dimethylbenzenesulfinic acid
 (d) ca. 9.5% 2-phenyl-2-propyl azide is formed.

not been corrected. Sample rate runs are given in Tables LXV, LXVI, LXVII and LXVIII and no drift is apparent. It is once more noted that the addition of 2,6-dimethylbenzenesulfinate has no appreciable effect on the ratio of rearrangement to solvolysis, and 2,6-lutidine causes a very small rate depression (Table VI).

Reaction in Anhydrous Acetic Acid

Acetolysis of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate was carried out at 25, 70 and 90° in the presence of sodium acetate. The reaction rate could not be measured by titrimetry for the following reasons. The 2,6-dimethylbenzenesulfinic acid, being a weak acid in anhydrous acetic acid, does not dissociate completely. This means that a buffered solution is obtained, (equation 1) and one is in effect titrating only a portion of the 2,6-dimethylbenzenesulfinic acid produced.



Further, a significant portion of the 2,6-dimethylbenzenesulfinic acid formed on solvolysis of the ester is consumed according to equation 2 to form 2,6-dimethylphenyl 2,6-dimethylbenzene thiol-sulfonate and 2,6-dimethylbenzenesulfonic acid (43). The sulfonic acid, being a relatively strong acid in the medium, also reacts with acetate ion according to equation 3, causing a further disappearance of acetate ion. The reaction rate was measured by following the appearance of

TABLE VI

SUMMARY ON SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
IN AQUEOUS DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE.

Run	Solvent, % dioxane	Ester, 10 ² M	Base ^a 10 ² M	10 ⁴ k, sec. ⁻¹	F _{solv.}	F _{rear.}
I-141	80	2.19	4.47	1.72 ± .04	.842	
I-142	80	2.19	4.47	1.73 ± .04		.187
I-145 ^b	80	2.19	9.64	1.74 ± .04	.849	
I-146 ^b	80	2.19	9.64	1.83 ± .11		.172
I-149	80	2.19	9.71	1.58 ± .04	.842	
I-150	80	2.19	9.71	1.72 ± .06		.177
I-113	90	2.13	4.67	.223 ± .012	.948	
I-114	90	2.13	4.67	.227 ± .013		.110
I-117 ^c	90	2.23	9.36	.219 ± .007	.953	
I-118 ^c	90	2.23	9.36	.213 ± .010		.107
I-121	90	2.22	9.64	.199 ± .009	.943	
I-122	90	2.22	9.64	.184 ± .016		.109

^a2,6-Lutidine.

^b2,6-dimethylbenzenesulfinic acid (.0240M) added.

^c2,6-dimethylbenzenesulfinic acid (.0260M) added.

2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. Even these measurements are subject to some error, as 2,6-dimethylphenyl 2,6-dimethylbenzene-thiolsulfonate is produced, which exhibits a strong absorption band at 1330 cm.⁻¹, very close to the sulfone peak being measured at 1308 cm.⁻¹ in carbon tetrachloride.

In contrast to the solvents previously studied, a change in the temperature of the acetolysis causes a small change in the amount of

sulfone formed as shown in Table VII. In the presence of about .055 M sodium acetate, 26% sulfone is formed at 25⁰, while 20 and 18% are formed at 70 and 90⁰ respectively. As shown in Table VII, both the rate of reaction and the fraction of sulfone formed are independent of the concentration of the added sodium acetate at 25⁰. Sample rate runs are given in Tables LXIX and LXX.

As shown in Tables VIII and IX, addition of lithium perchlorate at both 25 and 70⁰ causes a rate enhancement and a drop in the fraction of sulfone formed. The increase in rate observed upon addition of lithium perchlorate is not a linear one as illustrated in Figure V. At 25⁰ the "b" values obtained vary from 30 at .0048 M LiClO₄ to 120 at .2 M LiClO₄. The rate obeys the empirically derived relationship

$$k = k^0 (1 + 30 s + 400 s^2)$$

where k = observed rate constant in the presence of added lithium perchlorate, k^0 = the rate constant in the absence of added salt, and s = the molar concentration of added lithium perchlorate. This relationship is illustrated in Figure VI. A sample rate run is given in Table LXXI.

Addition of tetrabutylammonium bromide and tetrabutylammonium perchlorate (Run II-55, II-89, II-53 and II-87 in Table VIII) gave **rise to an increased rate of reaction and a lower amount of sulfone compared to** reaction in the absence of added salts. As shown in Figure V, up to .07 M salt concentration a linear increase in rate is observed. Under these conditions, the average "b" values for tetrabutylammonium bromide and tetrabutylammonium perchlorate are 8.5 and 10.5 respectively. Sample rate runs are given in Tables LXXII and LXXIII. A summary of

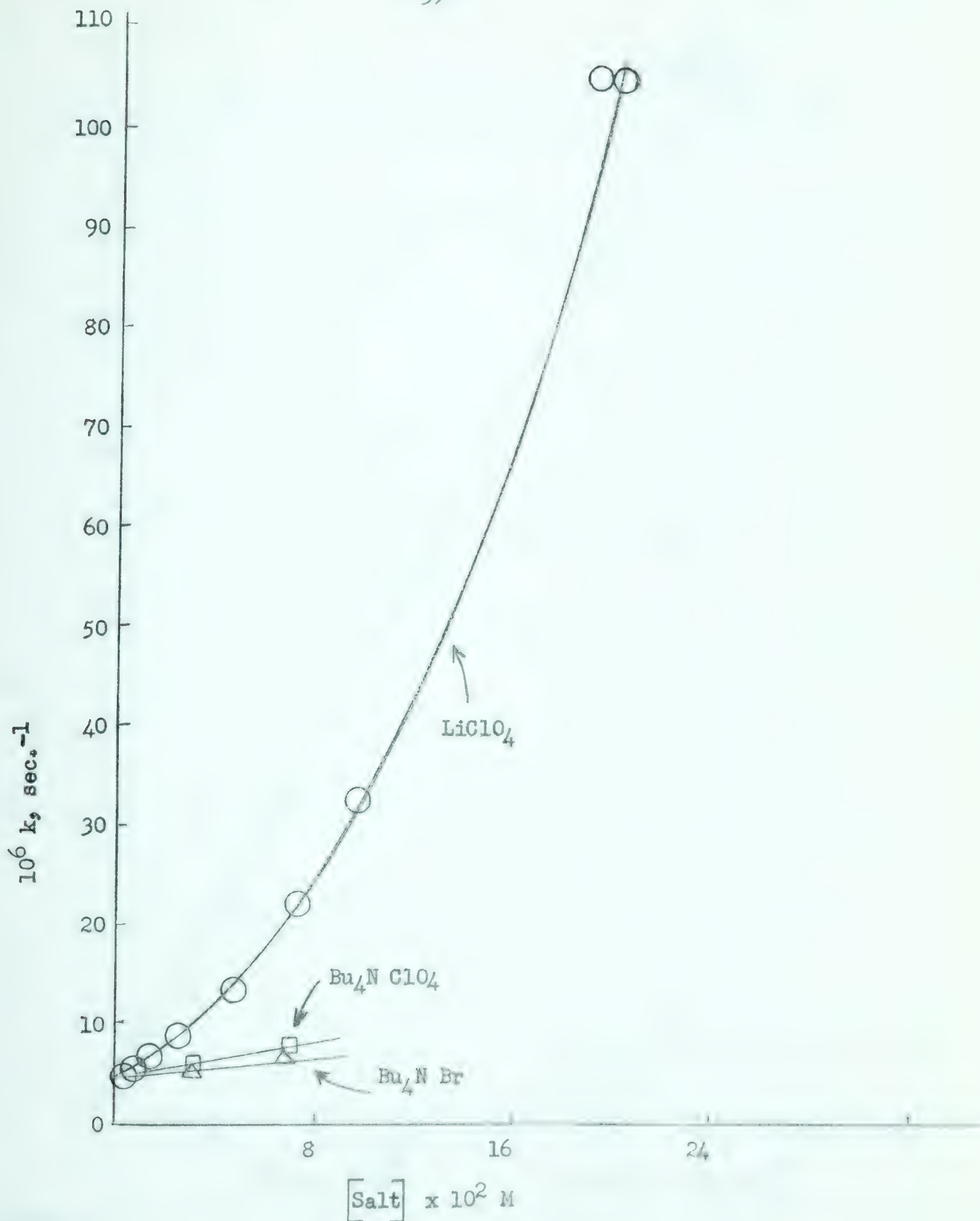


FIGURE V

The effect of salts on the rate of reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous acetic acid at 25° in the presence of added sodium acetate.

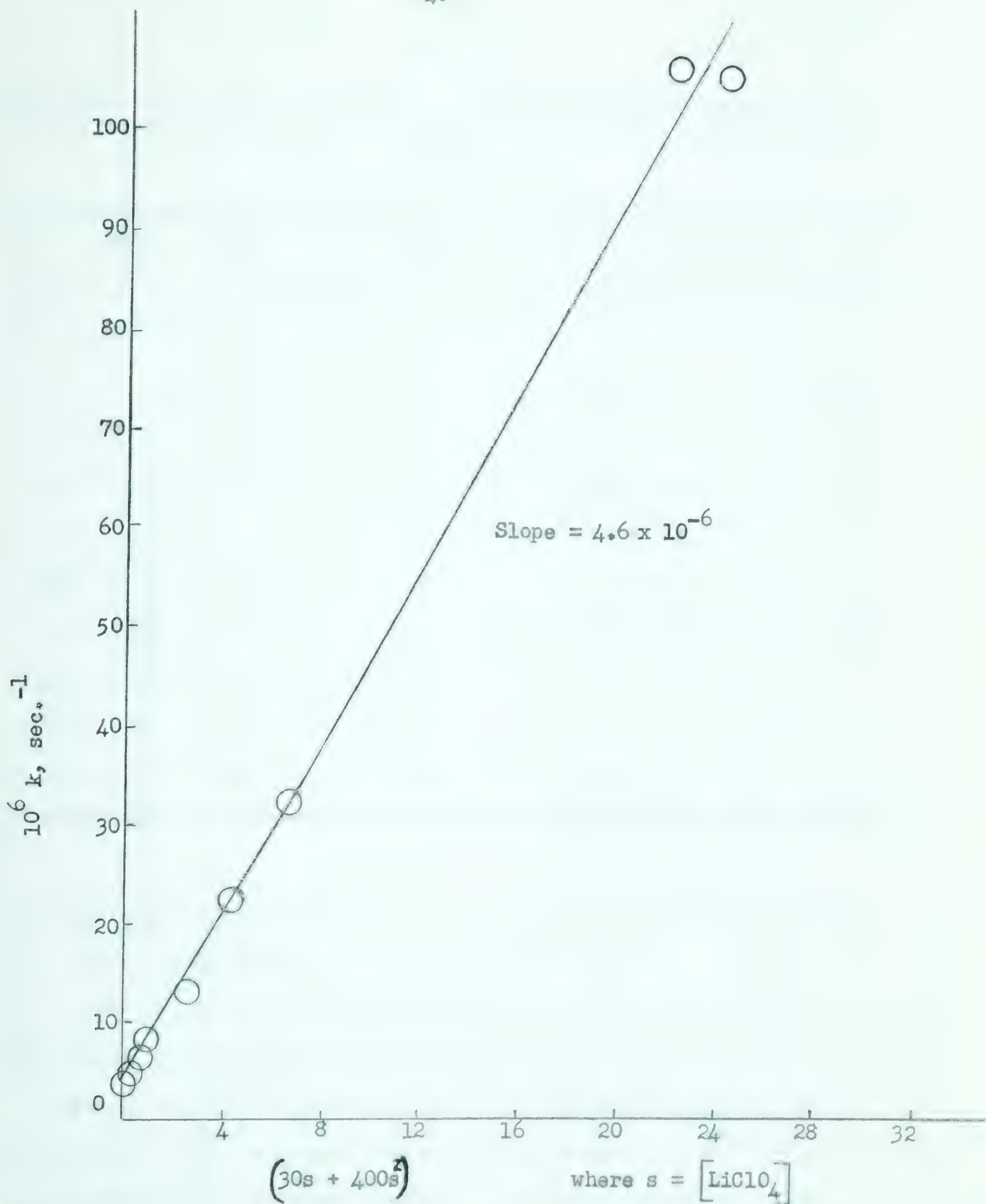


FIGURE VI

The effect of lithium perchlorate on the rate of reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous acetic acid at 25° in the presence of added sodium acetate.

TABLE VII

THE EFFECT OF TEMPERATURE ON THE ACETOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ACETIC ACID, WITH ADDED SODIUM ACETATE.

Run	Temp. °C	Ester 10 ² M	NaOAc 10 ² M	10 ⁶ k, sec. ⁻¹	F _{sulfone}
II-17	25	2.16	2.80	4.19 ± .21	.244
II-149	25	2.18	5.60	4.21 ± .09	.262
II-91	25	2.18	5.60	4.13 ± .13	.263
II-43	25	2.16	11.20	4.29 ± .14	.264
I-267	70	2.18	5.52	1670 ± 140	.203
I-284	70	2.15	5.52	1620 ± 80	.204
I-287	70	2.16	5.52	1540 ± 60	.201
I-255	90	2.19	5.52	5630 ± 150	
I-256	90	2.19	5.52	6040 ± 1450	.179
I-297	90	2.16	5.52	5890 ± 170	.182

rates carried out in acetic acid at 25 and 70° are presented in Tables VIII and IX respectively.

Solvolysis of 2-phenyl-2-propyl bromide in anhydrous acetic acid with added 2,6-dimethylbenzenesulfinic acid and sodium acetate was carried out at 25° for one hour. It has been reasoned earlier that solvolysis of the above bromide in anhydrous ethanol at 25° should be complete in one hour. Since anhydrous ethanol and anhydrous acetic acid have similar Y values, reaction of the bromide in acetic acid as well should proceed to completion in one hour. Measurement of the

TABLE VIII

SUMMARY ON SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM ACETATE.

Run No.	Ester 10 ² M	NaOAc 10 ² M	Added Salt	Conc. 10 ² M	10 ⁶ k ₁ sec. ⁻¹	F sulfone
II-17	2.16	2.80			4.19 ± .21	0.244
II-91	2.18	5.60			4.13 ± .13	.263
II-149	2.18	5.60			4.21 ± .09	.262
II-43	2.16	11.20			4.29 ± .14	.264
II-31	2.26	5.60	LiClO ₄	0.481	4.68 ± .33	.250
II-33	2.17	5.60	- ⁿ -	1.45	6.34 ± .20	.208
II-39	2.15	5.60	- ⁿ -	2.43	8.15 ± .42	.174
II-41	2.17	5.60	- ⁿ -	4.80	13.06 ± .32	.137
II-93	2.19	5.60	- ⁿ -	7.20	22.05 ± 1.02	.108
II-51	2.15	5.60	- ⁿ -	9.60	32.65 ± 1.86	.096
II-67	2.17	5.60	- ⁿ -	19.94	110 ± 4	.065
II-211	2.17	5.60	- ⁿ -	21.23	109 ± 3	.072
II-53	2.15	5.60	Bu ₄ N ClO ₄	3.16	5.48 ± .20	.244
II-87	2.20	5.60	- ⁿ -	7.06	7.62 ± .28	.200
II-89	2.15	5.60	Bu ₄ N Br	3.07	5.36 ± .25	.224
II-55	2.17	5.60	- ⁿ -	6.68	7.03 ± .29	.194

TABLE IX

SUMMARY ON SOLVOLYSIS OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ACETIC ACID AT 70.0° WITH ADDED SODIUM ACETATE (.0552 M).

Run No.	Ester 10 ² M	Added Salt	Conc. 10 ² M	10 ⁴ k sec. ⁻¹	F sulfone
I-267	2.18			16.7 ± 1.4	0.203
I-283	2.15			15.2 ± 0.5	
I-284	2.15			16.2 ± 0.8	.204
I-287	2.16			15.4 ± .6	.201
I-277	2.13	LiClO ₄	0.858	18.9 ± 1.1	.185
I-279	2.12	"	1.67	22.7 ± 1.3	.164
I-281 (a)	2.20	"	4.45	37.5 ± 2.2	.135
I-289	2.21	"	4.40	35.2 ± 1.0	.116
I-295	2.20	"	15.5	118 ± 25.0	.061

(a) NaOAc (.0836 M).

percentage transmittance near 1308 cm.^{-1} gave 0.61 and 0.30% sulfone from two experiments. Taking the higher value of 0.61%, this would correspond to no more than 2.5% of the sulfone formed in kinetic runs.

Product Analysis

A preliminary experiment showed that 2-phenylpropene and 2-phenyl-2-propyl ethyl ether could be separated by gas-liquid chromatography. A series of standards consisting of various ratios of olefin, ether and acetophenone (internal standard) were prepared, and analyzed in triplicate using a 2 meter "Perkin Elmer Column R (Ucon Oil 550)". Peak areas were calculated by multiplication of the peak height by the peak width at half the peak height. The area ratio of each component to the internal standard was calculated and plotted against the mole ratio of component to the internal standard. These results are given in Table X and Figure VII.

A synthetic mixture consisting of 2-phenyl-2-propyl 2,6-dimethyl-phenyl sulfone, 2-phenylpropene, 2-phenyl-2-propyl ethyl ether and 2,6-lutidine was dissolved in 100 ml. of anhydrous ethanol, transferred to a 160 ml. pressure bottle and heated for 12 hours (ca. 12 half-lives for the reaction of the corresponding arenesulfinate ester) in the 90° constant temperature bath. After cooling, the reaction mixture was carried through the same extraction procedure as used in kinetic runs. The solvent was carefully removed, and the residual oil chromatographed on alumina.

To the first fraction obtained from **the chromatogram, a known** amount of acetophenone was added, and aliquots of the solution were analyzed by gas-liquid chromatography as described above. From the area

TABLE X

ANALYSES OF SYNTHETIC MIXTURES OF 2-PHENYLPROPENE, 2-PHENYL-2-PROPYL
ETHYL ETHER, USING ACETOPHENONE AS INTERNAL STANDARD.

Operating Conditions: 2 Meter Column Perkin Elmer R (Ucon Oil 550);
Column Temperature: 170°; Column Pressure (Helium): 25/5.6 (gauge
pressure); Detector Voltage: 8 V .

Sample No.	Components	Weight in g.	Calculated mole ratio.	Found average area ratio.
I	Olefin (a) Ether (b) Acetophenone (c)	0.151 .103 .273	0.544 .276	0.551 .284
II	Olefin Ether Acetophenone	.225 .201 .225	.993 .652	.998 .669
III	Olefin Ether Acetophenone	.253 .155 .226	1.100 .501	1.111 .518
IV	Olefin Ether Acetophenone	.183 .282 .227	.792 .908	.818 .906
V	Olefin Ether Acetophenone	.138 .236 .228	.595 .757	.634 .765
VI	Olefin Ether Acetophenone	.091 .177 .235	.381 .550	.413 .568

(a) 2-Phenylpropene, retention time: 250 sec.

(b) 2-Phenyl-2-propyl ethyl ether, retention time: 445 sec.

(c) Acetophenone, retention time: 525 sec.

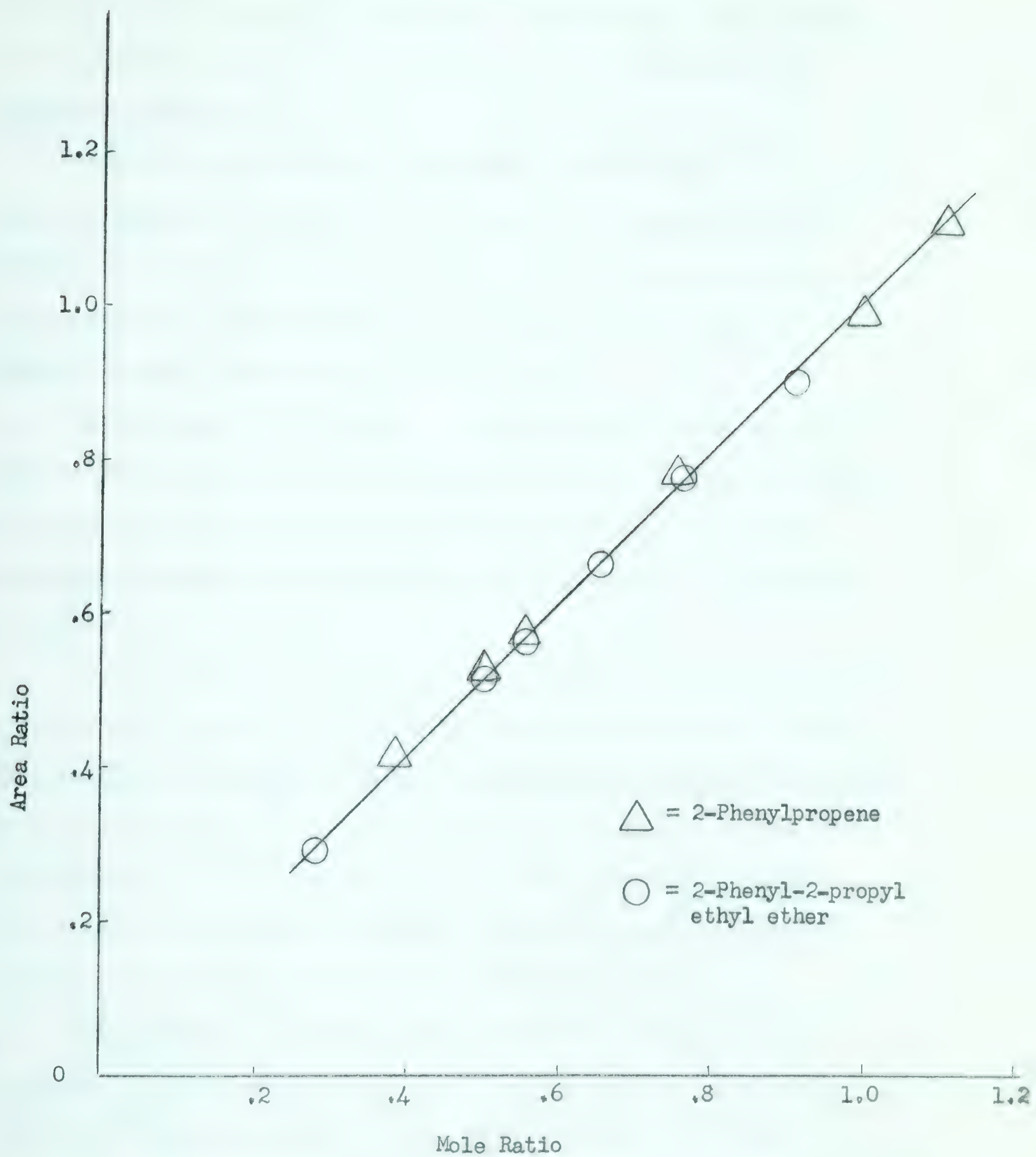


FIGURE VII

Calibration curve for gas liquid chromatography of 2-phenyl-2-propyl ethyl ether and 2-phenylpropene, using acetophenone as internal standard.

ratios obtained, the moles of components could be calculated by the use of the calibration curve Figure VII, and the values obtained are recorded in Table XI.

From the second fraction obtained by chromatography, (eluted with 15% ether-pentane), the solvent was removed and the residual solid material was recrystallized from pentane. Its infrared and n.m.r. spectra and m.p. corresponded to those of an authentic sample of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone.

The procedure for the actual product run was the same as in the model run described above, except 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate and 2,6-lutidine were weighed out initially. The results obtained in anhydrous ethanol at 90° and 80% ethanol at 70° are shown in Table XII.

In run I-226 in 80% ethanol at 70° a slight modification in workup procedure was necessary. In the solid-liquid chromatography on alumina three fractions were taken. The first **fraction was treated in the usual** manner and the amount of olefin and ether were determined by gas-liquid chromatography. From the middle fraction, the sulfone was isolated, while removal of the solvent from the last fraction gave 2-phenyl-2-propanol which was identified by its infrared spectrum.

Good agreement is found between percentage solvolysis and rearrangement values obtained from kinetic runs and the results of product isolation experiments. In anhydrous ethanol at 90°, from kinetic runs, 90.5% solvolysis and 9.5% rearrangement was observed, while in product runs 89.0% solvolysis and 9.6% rearrangement product, sulfone, was isolated. In 80% ethanol from kinetic runs 84.5%

TABLE XI

CONTROL ON THE ISOLATION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE, 2-PHENYLPROPENE AND 2-PHENYL-2-PROPYL ETHYL ETHER IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE.

Compound	Weight in g.	Initial moles, 10 ³	Recovered moles, 10 ³	% Recovery
Sulfone	0.0622	0.216	0.210(a)	97.0
Olefin	.0886	.751	.734(b)	97.4
Ether	.1816	1.107	1.095(b)	99.0
2,6-Lutidine	.4728	4.411	—	—

(a) Measured gravimetrically. (b) Measured by g.l.c.

TABLE XII

SUMMARY OF PRODUCT RUNS CARRIED OUT ON 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN THE PRESENCE OF ADDED 2,6-LUTIDINE.

Compound	Percentage of Product Isolated:		
	Run I-208 100% EtOH at 90.0°	Run I-217 100% EtOH at 90.0°	Run I-226 80% EtOH at 70.0°
2-Phenylpropene (a)	38.0	38.0	32.7
2-Phenyl-2-propyl ethyl ether (a)	51.0	50.8	41.2
2-Phenyl-2-propyl 2,6-dimethylphenyl sulfone (b)	9.7	9.6	16.2
2-Phenyl-2-propanol (b)	—	—	9.1
Percentage starting material accounted for:	98.7	98.4	99.2

(a) Measured by g.l.c.

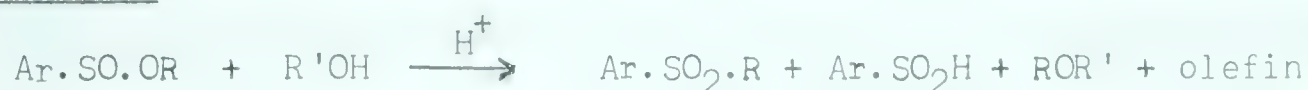
(b) Measured gravimetrically.

solvolysis and 15.7% rearrangement product was observed, while in the product run I-226, 83.0% solvolysis products and 16.2% rearrangement product, sulfone, was isolated.

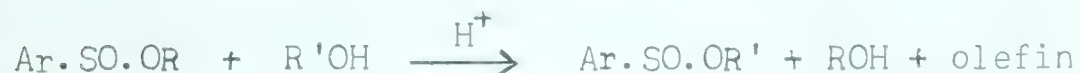
DISCUSSION

Arenesulfinate esters can undergo solvolysis with either carbon-oxygen or sulfur-oxygen bond cleavage or by a combination of both. These reactions may take place under acid-catalyzed, base-catalyzed or neutral conditions as illustrated below.

Acid Catalysis



or

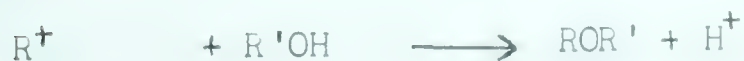
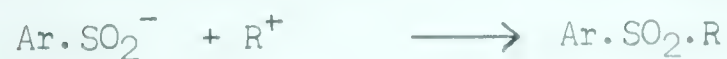


where R' = H or alkyl, R'OH = solvent

Base Catalysis



Neutral Ionization



It has been shown in these laboratories (15,16) that the presence of two methyl groups adjacent to the sulfur atom of the arenesulfinate ester considerably hinders attack upon that atom. In refluxing ethanol with added sodium acetate more than ninety per cent of isopropyl 2-methylbenzenesulfinate is converted to the ethyl ester in 48 hours. In contrast, only five per cent reaction in 51 hours and ten per cent

reaction in 190 hours of isopropyl 2,6-dimethylbenzenesulfinate takes place under identical conditions (15). To diminish further the possibility of sulfur-oxygen bond cleavage, 2,6-lutidine was used as the added base in most of the solvolyses. The presence of two methyl groups adjacent to the nitrogen atom of 2,6-lutidine should make it a relatively poor nucleophile, decreasing the possibility of attack on the sulfur atom of the arenesulfinate ester (16). The use of 2,6-lutidine as the added base offers two other advantages. It is soluble in a variety of organic solvents as well as in mixed aqueous organic solvents. A mixture of 2,6-lutidine and 2,6-lutidinium ion forms a buffered solution which can be titrated in a manner similar to acetic acid in the presence of acetate ion. Noreyko (16) found that *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate reacts with a rate constant of $6 \times 10^{-9} \text{ sec.}^{-1}$ in anhydrous ethanol at 90° in the presence of 2,6-lutidine, and $1.3 \times 10^{-7} \text{ sec.}^{-1}$ in the presence of pyridine. When potassium acetate is the added base (ca. .05 M), under the same conditions a rate constant of ca. $8 \times 10^{-6} \text{ sec.}^{-1}$ is obtained. The product of the above reaction in each case is ethyl 2,6-dimethylbenzenesulfinate.

One can rule out sulfur-oxygen bond cleavage in the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate on the basis of the following evidence. Reaction of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate with ethoxide ion is about twice as fast as the reaction of isopropyl 2,6-dimethylbenzenesulfinate under comparable conditions (16). This would suggest that sulfur-oxygen bond cleavage should be slightly more favored in a primary than a secondary sulfinate ester. Since a tertiary alkoxide would be a poorer leaving group than a primary or a secondary, sulfur-oxygen bond cleavage in a tertiary alkyl

2,6-dimethylbenzenesulfinate should be no faster than with *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate. 2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate is an aralkyl system and the phenyl group would be likely to speed up the reaction compared to a hydrogen. One could anticipate that the acceleration by the phenyl group would more than outweigh the rate retardation by the two methyl groups. Thus, sulfur-oxygen bond cleavage for 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate would be faster than with *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate, and the above estimate may be a minimum estimate of the rate of sulfur-oxygen bond cleavage. The observed rate constant for the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° in the presence of 2,6-lutidine is $2.2 \times 10^{-4} \text{ sec.}^{-1}$ or 3×10^4 faster than the reaction of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate under the same conditions.

An alternate model compound for sulfur-oxygen bond cleavage could be benzyl 2,6-dimethylbenzenesulfinate. The rate constant for this compound in anhydrous ethanol at 90° in the presence of 2,6-lutidine is ca. $2 \times 10^{-7} \text{ sec.}^{-1}$ (63). The reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate is 10^3 times faster than that of benzyl 2,6-dimethylbenzenesulfinate under the same conditions. Since the two methyl groups in the 2-phenyl-2-propyl system would be expected to slow down the reaction, the above must be a maximum estimate for the rate of sulfur-oxygen bond cleavage in 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. Therefore by comparison of the rate of sulfur-oxygen bond cleavage in *p*-methoxyneophyl and benzyl 2,6-dimethylbenzenesulfinate, we have bracketed the process in 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate.

If a base-catalyzed reaction were taking place, then an increase in the 2,6-lutidine concentration would be expected to give rise to increased rate of reaction. Instead, tripling of the 2,6-lutidine concentration results in a very small rate depression. Thus base catalysis is considered to be of negligible importance in these reactions.

Similar conclusions can be derived by examination of the reaction products. The expected products from sulfur-oxygen bond cleavage in ethanol would be ethyl 2,6-dimethylbenzenesulfinate and 2-phenyl-2-propanol, and no change in acid titer should take place. Solvolysis of the arenesulfinate ester in ethanol yields 2-phenylpropene, 2-phenyl-2-propyl ethyl ether and 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. The formation of olefin and ether is accompanied by the production of 2,6-dimethylbenzenesulfinic acid. The above products could not be formed by sulfur-oxygen bond cleavage but must be the result of carbon-oxygen bond cleavage. Therefore, on the basis of both kinetic data and the results of product isolation, sulfur-oxygen cleavage is insignificant in the solvolysis of the arenesulfinate ester in ethanol.

Bunton and Hendry (44) have shown that under initially neutral conditions the reaction of benzhydryl 4-methylbenzenesulfinate is autocatalytic due to acid produced in the solvolysis of the arenesulfinate ester. Under our experimental conditions 2,6-lutidine is present, and autocatalysis is not observed in the solvolysis of the arenesulfinate ester. Further, addition of 2,6-dimethylbenzenesulfinic acid (with excess 2,6-lutidine) at the start of the reaction gave rise only to a slight increase in rate, $b = 6.1$, which is of the order expected for a normal salt effect (24).

The above line of reasoning holds equally well for the reaction in 80% ethanol. In this solvent there is about 9% 2-phenyl-2-propanol formed, which could arise by either carbon-oxygen or sulfur-oxygen bond cleavage. If the 2-phenyl-2-propanol were formed by sulfur-oxygen bond cleavage, attack on the arenesulfinate ester would have to be carried out by water or ethanol as illustrated.



or



p-Methoxyneophyl 2,6-dimethylbenzenesulfinate has a rate constant of $7.2 \times 10^{-8} \text{ sec.}^{-1}$ in 60% ethanol and $6 \times 10^{-9} \text{ sec.}^{-1}$ in anhydrous ethanol at 90° in the presence of 2,6-lutidine(16). Therefore, the rate of sulfur-oxygen bond cleavage in 80% ethanol should be no faster than $7.2 \times 10^{-8} \text{ sec.}^{-1}$. The rate constant for 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate measured in 80% ethanol at 90° is $2 \times 10^{-3} \text{ sec.}^{-1}$ or 3×10^4 faster than that found for p-methoxyneophyl 2,6-dimethylbenzenesulfinate in 60% ethanol. Ethyl 2,6-dimethylbenzenesulfinate was not detected in the products from the reaction. Therefore the 2-phenyl-2-propanol must have been formed by carbon-oxygen bond cleavage, and sulfur-oxygen bond cleavage is also unimportant in solvolysis of the arenesulfinate ester in 80% ethanol.

There are no data available on sulfur-oxygen bond cleavage of arenesulfinate esters in aqueous dioxane in the presence of weak bases. Sulfur-oxygen bond cleavage in the presence of 2,6-lutidine is speeded up by aqueous solvents (16). In the absence of a better comparison, we

may assume that the rate of sulfur-oxygen bond cleavage in 80 and 90% dioxane should be about the same as that found in 60% ethanol for *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate, since 80 and 90% dioxane are poorer ionizing solvents than 60% ethanol (51). The observed rate constants of 1.7×10^{-4} and 2×10^{-5} sec.⁻¹ in 80 and 90% dioxane in the presence of 2,6-lutidine at 90°, are 2350 and 280 times that found in 60% ethanol for *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate. Therefore sulfur-oxygen bond cleavage is unlikely to be of significance in the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in aqueous dioxane.

Since doubling of the added 2,6-lutidine concentration results only in a very small rate depression, a base-catalyzed reaction cannot be taking place. Autocatalysis due to acid produced is not observed in the reactions of the arenesulfinate ester in aqueous dioxane, therefore, an acid-catalyzed reaction is unlikely as well.

Thus the process being measured in these four solvents is the carbon-oxygen bond fission of the arenesulfinate ester. It is apparent that concurrent solvolysis and rearrangement takes place in each of the above mentioned solvents.

In the acetolysis of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate the observed rate is independent of the concentration of the added sodium acetate. On this basis a base-catalyzed reaction of the arenesulfinate ester is ruled out. The effect of added 2,6-dimethylbenzenesulfinic acid could not be studied due to its decomposition which results in the formation of sulfonic acid and thiolsulfonate.

In general, solvolyses in anhydrous acetic acid and anhydrous

ethanol proceed at nearly the same rate. For example, α -phenylethyl chloride solvolyzes ca. twice as fast at 50° in anhydrous ethanol as in anhydrous acetic acid (37). p-Methoxyneophyl p-toluenesulfonate reacts 2.8 times faster in anhydrous acetic acid than in anhydrous ethanol (45). In contrast, reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in acetic acid is 25 times faster at 90°, 33 times faster at 70° and 35 times faster at 25° than in anhydrous ethanol. Benzhydryl 2,6-dimethylbenzenesulfinate solvolyzes in acetic acid at 90° forty times faster than in anhydrous ethanol at the same temperature (46). In the acetolysis of p-chlorobenzhydryl chloride considerable ion pair return takes place, thus racemization is faster than acetolysis by factors of ca. 30-70 (47). Winstein, Fainberg and Grunwald (48) have suggested that in the acetolysis of benzhydryl chloride, the ionization rate is at least 10 times the titrimetric rate, while in the acetolysis of the corresponding bromide the ionization rate is 15-20 times the titrimetric rate. Thus the apparently enhanced rate of acetolysis of the arene-sulfinate ester may only reflect a slower than normal rate observed with the chlorides.

Darwish and McLaren (46) have proposed that specific solvation of the 2,6-dimethylbenzenesulfinate leaving group may be responsible for a portion of the increased rate of reaction. Specific solvation of the leaving fluoride group has been suggested in the solvolysis of benzhydryl fluoride (48). Acetolysis of this compound is about 10^5 times faster than **reaction in anhydrous ethanol.** A major portion of the rate enhancement observed with benzhydryl fluoride is most likely due to hydrogen bonding between the leaving fluoride group and the solvent (48).

A further indication of strong interaction between fluoride and a proton donor in solvolysis, is the autocatalysis observed in the solvolyses of substituted benzyl fluorides (49). Autocatalysis has not been noted in the reactions of the corresponding chlorides and bromides. Catalysis by strong acids is noted in the solvolysis of substituted benzyl fluorides. In a similar manner, strong acids accelerate the solvolysis of sulfinates (44). The observations of sulfone formation, relatively fast rate of reaction and an accelerated rate of reaction in acetic acid compared to ethanol, suggest that carbon-oxygen bond cleavage must be taking place. In all cases solvolysis arises by carbon-oxygen bond cleavage and must involve carbonium ion species of some type.

Sulfone formation could take place by three distinct reaction paths which are: (i) a concerted cyclic rearrangement not involving ionic species, (ii) ion pair return, (iii) recombination of dissociated ions.

Two of the possible modes of sulfone formation involve ionic species, while one does not. A clear distinction between these processes can be made by an examination of the changes in the rate of reaction on changing the ionizing power of the solvent. In the two ionic processes an increase in the ionizing power of the solvent is expected to be reflected by an increased rate of reaction. A concerted cyclic rearrangement not involving ionic species would be insensitive to changes in the ionizing power of the solvent. **A suitable model for the ionization of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate** would be the corresponding chloride. Unfortunately, there are only data available on the rate of

reaction of 2-phenyl-2-propyl chloride in 90% acetone, and none in those solvents in which the arenesulfinate ester was solvolyzed. An alternative model for the ionization of the 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate would be α -phenylethyl chloride. However, ion pair return may be taking place in the reactions of α -phenylethyl chloride and the extent of return may vary from solvent to solvent. Therefore, changes in solvolysis rate may not be accurately reflected by changes of the ionization rate. Reaction of the above chloride is 45 times faster at 25° and 35 times faster at 50° in 80% ethanol than in anhydrous ethanol (50). The solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate has been suggested as a model to be used in rearranging systems. The above compound solvolyzes 7.8 times faster at 25° and 6.2 times faster at 50° in 80% ethanol than in anhydrous ethanol (45). In comparison, reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate is 6.5 times faster at 70° and 9 times faster at 90° in 80% ethanol than in anhydrous ethanol. The plot of log *k*'s of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate disappearance, solvolysis and sulfone formation against the log of the rate constant of α -phenylethyl chloride and *p*-methoxyneophyl *p*-toluenesulfonate in a number of solvents is given in Figures VIII and IX, and the data are also tabulated in Table XIII. The slopes of the lines of log *k*'s of ester disappearance, solvolysis and sulfone formation against log *k*_{solv.} of α -phenylethyl chloride are .71, .70 and .77, while against log *k*_{solv.} of *p*-methoxyneophyl *p*-toluenesulfonate they are 1.07, 1.10 and 1.19 respectively. It is apparent that the rates of both solvolysis and sulfone formation reflect a similar sensitivity to ionizing power of the solvent. (In both plots the point for acetolysis is out of line, i.e., reaction is ca. 100 and 10 times faster than expected.) The linear relationship between log *k*'s in the present system and those of α -phenylethyl and *p*-methoxyneophyl

very strongly suggests a pathway involving ionization to be the principal route of reaction for 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. The almost parallel lines obtained for ester disappearance, solvolysis and sulfone formation indicate that both solvolysis products and sulfone are affected almost to the same extent by changes in the ionizing power of the solvent. An increase in the ionizing power of the solvent increases the rate of reaction and the amount of rearrangement product, sulfone, formed. These results indicate that the transition states for both solvolysis and rearrangement must be very similar. Since the structure of the transition state for solvolysis must be close to that of the carbonium ion, the transition state for the rearrangement must also be close to that of the carbonium ion. Hence, we will consider both species as produced by a carbonium ion reaction.

It is noteworthy that in the plots of $\log k_{\text{solv.}}$ and $\log k_{\text{rear.}}$ for the arenesulfinate ester against $\log k_{\text{solv.}}$ for α -phenylethyl chloride or *p*-methoxyneophyl *p*-toluenesulfonate (Figures VIII and IX), the point for acetolysis is off the line by the same amount for both solvolysis and rearrangement. Therefore, both solvolysis and rearrangement are affected to the same extent in acetolysis. Thus, whatever the detailed explanation for the deviation of the acetolysis point from the lines may be, both solvolysis and rearrangement deviate by the same amount. Therefore, the apparent discrepancy of the acetolysis point indicates a very similar transition state for solvolysis and rearrangement and both proceed by carbonium ion processes.

An examination of substituent effects also provides valuable information on the type of reaction taking place. In anhydrous ethanol

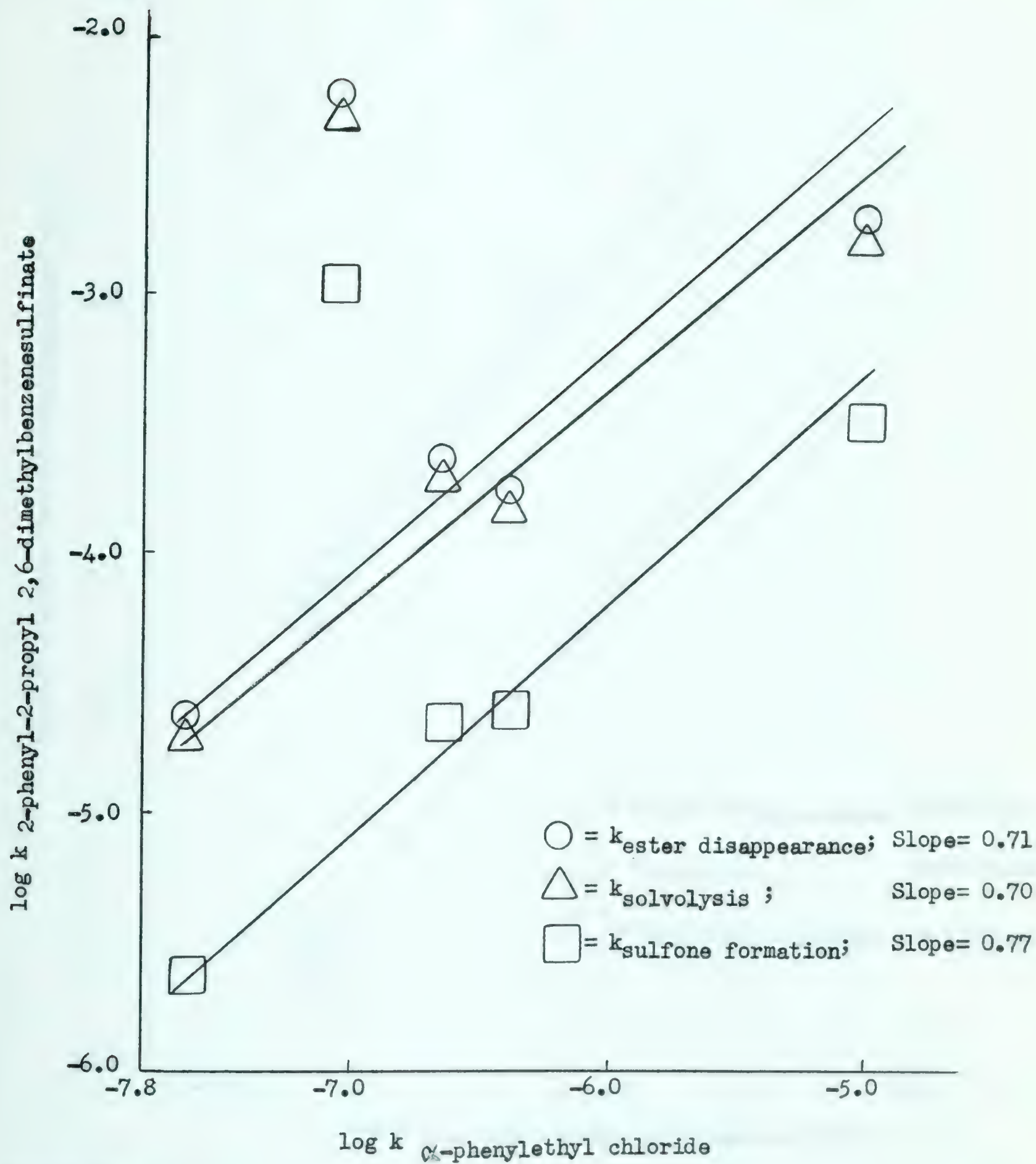


FIGURE VIII

Relationship between log k's for ester disappearance, solvolysis and sulfone formation for 2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate (90.0°) against the log $k_{\text{solv.}}$ for α -Phenylethyl chloride (25.0°).

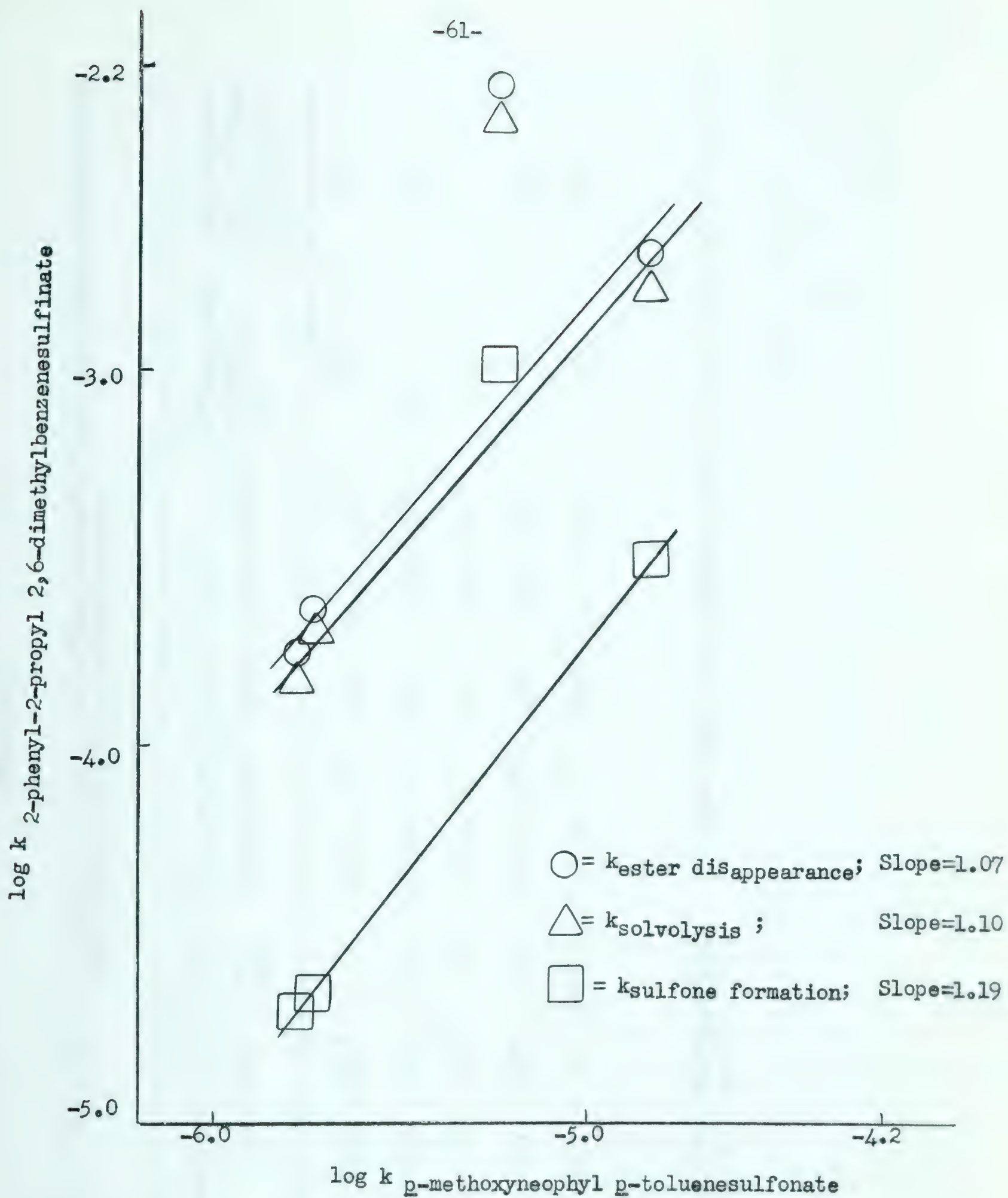


FIGURE IX

Relationship between log k's for ester disappearance, solvolysis and sulfone formation for 2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate (90.0°) against the log $k_{\text{solv.}}$ for p-Methoxyneophyl p-toluenesulfonate (25.0°).

TABLE XIII

RELATIVE RATES OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE, α -PHENYLETHYL CHLORIDE AND p-METHOXYNEOPHYL p-TOLUENESULFONATE.

Solvent	$k_{\text{obs.}}, \text{sec.}^{-1}$	rel. rate	$k_{\text{solv.}}, \text{sec.}^{-1}$	Frear.	$k_{\text{rear.}}, \text{sec.}^{-1}$	α -Phenylethyl chloride at 25.0° (a)	p-Methoxyneop- hyl p-toluene sulfonate at 25.0° (b)
Anhyd. EtOH	2.25×10^{-4}	1	2.03×10^{-4}	.095	2.14×10^{-5}	1 (c)	1 (d)
80% EtOH	2.03×10^{-3}	9.05	1.71×10^{-3}	.157	3.20×10^{-4}	45.5	7.9
90% Diox.	2.20×10^{-5}	.10	1.96×10^{-5}	.109	2.40×10^{-6}	.1	
80% Diox.	1.7×10^{-4}	.75	1.40×10^{-4}	.179	3.05×10^{-5}	1.79	.89
Anhydrous Acetic Acid	5.9×10^{-3}	26.2	4.8×10^{-3}	.180	1.1×10^{-3}	.40	2.96

(a) Data taken from reference (50). (b) Data taken from reference (45). (c) $k_1 = 2.16 \times 10^{-7} \text{ sec.}^{-1}$
 (d) $k_1 = 1.79 \times 10^{-6} \text{ sec.}^{-1}$

at 25° in the presence of 2,6-lutidine 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate reacts 17,000 times faster than 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. (Data from Chapter II.) This is of the order expected for an ionization reaction, as 2-p-methoxyphenyl-2-propyl chloride solvolyzes 3300 times faster than 2-phenyl-2-propyl chloride in 90% acetone at 25° (26). The effects of both solvents and substituents on the rate of reaction clearly indicate that sulfone formation takes place by an ionic type mechanism (either by ion pair return, or recombination of dissociated ions) and not by a concerted cyclic non-ionizing rearrangement.

The fraction of sulfone formed within any run was constant. Addition of 2,6-dimethylbenzenesulfinate ion does not give rise to common ion rate depression. If sulfone were formed from free ions, the rate of sulfone formation from the carbonium ion would be a second-order process, while the rate of solvolysis is a pseudo first-order reaction. Added 2,6-dimethylbenzenesulfinate ion would be expected to compete with the solvent for the intermediate carbonium ion, resulting in an increased amount of sulfone, and decreased amounts of solvolysis products formed. Addition of 2,6-dimethylbenzenesulfinate ion has no effect on the ratio of solvolysis to rearrangement products formed. Therefore, sulfone formation does not arise from dissociated ions.

Exchange experiments also give evidence for sulfone arising via an intramolecular pathway. Solvolysis of 2-phenyl-2-propyl bromide in the presence of 2,6-dimethylbenzenesulfinate ion in anhydrous ethanol gives rise to a maximum of 0.65% 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, which is equivalent to 7.5% of the sulfone formed in any of the

kinetic runs. 2-Phenyl-2-propyl bromide on ionization should give rise to the same cation as 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. If the ionization of the two species gave the same relative amounts of ion pairs and free ions, and sulfone is produced exclusively from free ions the same amount of sulfone should result from each. Since 2-phenyl-2-propyl bromide gives a maximum of 0.65% sulfone, these results indicate that sulfone does not arise from dissociated ions.

When solvolysis of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate is carried out in the presence of tetrabutylammonium 2-methylbenzenesulfinate, the sulfone formed is exclusively 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. If a significant amount of exchange between the ion pair species and tetrabutylammonium 4-methylbenzenesulfinate had taken place, 2-phenyl-2-propyl 4-methylphenyl sulfone should have been formed. Since neither common ion rate depression nor exchange is observed, sulfone formation must occur by ion pair return (4).

Turning to an examination of salt effects, addition of both lithium perchlorate and tetrabutylammonium perchlorate in ethanol gives rise to a linear increase in rate, known as a normal salt effect. Since neither the rate of formation, nor the yield of sulfone is affected by the addition of these salts, they have little, if any, effect on ion pair return.

We next proceeded to evaluate the effect of a number of nucleophiles on the rate of formation and the yield of sulfone.



If exchange took place between the arenesulfinate ester and tetrabutylammonium bromide, 2-phenyl-2-propyl bromide would be expected to be

formed. It has been shown that solvolysis of 2-phenyl-2-propyl bromide in the presence of 2,6-dimethylbenzenesulfinate ion gives rise to a negligible amount of sulfone. Thus, if exchange had taken place, lower amounts of sulfone would be expected to be formed in solvolysis of the ester in the presence of tetrabutylammonium bromide. Since the same amount of sulfone is formed both in the presence and absence of tetrabutylammonium bromide within experimental error, no exchange could have taken place between the arenesulfinate ester and tetrabutylammonium bromide.

Erratic and non-reproducible titers were obtained in the solvolysis of the ester in ethanol in the presence of added potassium thiocyanate. However, the usual amount of sulfone was formed and no absorption due to either 2-phenyl-2-propyl thiocyanate or 2-phenyl-2-propyl isothiocyanate was detected in the infrared between 3000 and 2000 cm^{-1} . Thus, exchange has not been detected with either bromide or thiocyanate in ethanol solution.

Solvolysis of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol in the presence of tetrabutylammonium azide gave rise to lower infinity titers and lesser amounts of sulfone than in the absence of added salt. On varying the concentration of the added quaternary azide, a maximum of 25% 2-phenyl-2-propyl azide was obtained. These results are discussed in detail in Chapter II.

It has been shown that an increase in the ionizing power of the solvent increases the rate of reaction and the amount of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone formed. The increase in the yield of sulfone upon increasing the ionizing power of the solvent could be due

to further dissociation of ion pairs once they are formed, or it could arise by an additional mode of formation involving free arenesulfinate ion. The increased yields of sulfone upon increasing the ionizing power of the solvent could also be due to variations of the nucleophilicity of the solvents. All of the above results are consistent with ion pairs as intermediates for sulfone formation.

Finally, one may consider certain observations on the stability of 2,6-dimethylbenzenesulfinic acid in anhydrous ethanol in the presence of tetrabutylammonium bromide and 2,6-lutidine.

The titer of 2,6-dimethylbenzenesulfinic acid (.02 M) in the presence of 2,6-lutidine and tetrabutylammonium bromide (.036 M) in anhydrous ethanol at 90° decreased significantly (Table LI). In the time corresponding to ten half-lives of the arenesulfinate ester 7.5 per cent, and in the time corresponding to twenty half-lives of the arenesulfinate ester 13.5 per cent decrease of the initial acid titer was observed, and ethyl 2,6-dimethylbenzenesulfinate was formed. This reaction has not been extensively investigated, but the acid titer seems to approach a constant value. The following mechanism is consistent with the experimental observations:



The formation of small amounts of ethyl 2,6-dimethylbenzenesulfinate (from esterification of the acid produced) could not be demonstrated in the solvolysis of the arenesulfinate ester as both 2-phenylpropene and the ethyl ester show absorption in the infrared in the vicinity of 900 cm.⁻¹. The rate constants measured by titrimetry

showed a slight upward drift, while those measured by infrared spectrophotometry were constant. When corrections were applied (from appropriate control runs) for the disappearance of 2,6-dimethylbenzenesulfinic acid by the formation of ethyl 2,6-dimethylbenzenesulfinate, good agreement was noted between rate constants measured by titrimetry and infrared spectrophotometry.

CHAPTER II

THE REACTIONS OF PARA-SUBSTITUTED 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENE

SULFINATES

INTRODUCTION

From a study of solvent effects we have shown that both solvolysis and sulfone arise from ionic intermediates. To gain further information on the mechanism of the reaction, a study of substituent effects was started. Accordingly, we have synthesized the 2,6-dimethylbenzene-sulfinate of 2-p-tolyl-2-propanol, 2-p-bromophenyl-2-propanol, 2-p-methoxyphenyl-2-propanol and 2-p-nitrophenyl-2-propanol. Reaction of these arenesulfinate esters was studied in ethanol and a number of other solvents. The effect of added salts was evaluated, most of the work being done on 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate. The results of product isolation of the various arenesulfinate esters in anhydrous ethanol are given, with the exception of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate. A correlation between the rates observed and the modified Hammett relationship $\rho\sigma^+$ has been also found. A discussion of sulfone formation in various arenesulfinate esters is given.

RESULTS

Preparations

The reaction between p-bromoacetophenone and methylmagnesium iodide resulted in the formation of 2-p-bromophenyl-2-propanol. In a

similar manner, 2-p-tolyl-2-propanol and 3-phenyl-3-pentanol were prepared. The treatment of p-methoxyacetophenone with methylmagnesium iodide did not yield significant amounts of 2-p-methoxyphenyl-2-propanol. The latter compound was prepared by the reaction between p-methoxyphenylmagnesium bromide and acetone. Nitration of 2-phenylpropane resulted in a mixture of 2-(p-nitrophenyl)propane and 2-(o-nitrophenyl)propane. Oxidation of this material by the method of Kwart (55), using chromic acid in a mixture of acetic acid and acetic anhydride, followed by chromatography on alumina, yielded the desired 2-p-nitrophenyl-2-propanol. Some of the pertinent physical properties of these alcohols are listed in Table XIV, while their n.m.r. spectra are summarized in Table XV. Unless otherwise specified, in the tabulation of n.m.r. spectra the relative integrated areas of a compound agree with the theoretical values.

Treatment of 2-p-bromophenyl-2-propanol with phosphoric acid overnight at 90° gave rise to 2-p-bromophenylpropene. In an analogous manner, 2-p-tolyl-2-propanol afforded 2-p-tolylpropene. Treatment of 2-p-methoxyphenyl-2-propanol with sulfuric acid for three minutes on the steam bath yielded after purification 2-p-methoxyphenylpropene.

Treatment of the above mentioned alcohols with anhydrous ethanol in the presence of catalytic amounts of sulfuric acid yielded the respective ethyl ethers. The physical properties of the olefins and ethyl ethers prepared are listed in Table XVI, while their n.m.r. spectra are summarized in Tables XVII and XVIII.

Treatment of 2-p-bromophenyl-2-propanol with 2,6-dimethylbenzenesulfinic acid in formic acid containing sodium formate, gave rise to

TABLE XIV

PHYSICAL PROPERTIES OF SOME 2-ARYL-2-PROPANOLS

Compound	b.p.	n_D^{25}	Hydroxyl infrared band, (CS ₂)	Reported physical properties, reference
2-Phenyl-2-propanol	68-70°(4.2 mm.)	1.5188	3580, 3480 cm. ⁻¹	b.p. 94°(13 mm.) (52)
2- <i>p</i> -Bromophenyl-2-propanol	104-107°(1.6 mm.) m.p. 45-46°		3580 cm. ⁻¹	m.p. 45.6° (53)
2- <i>p</i> -Tolyl-2-propanol	70-72°(2 mm.)	1.5168	3580, 3480 cm. ⁻¹	b.p. 101°(10 mm.) n_D^{20} 1.5180 (39)
2- <i>p</i> -Methoxyphenyl-2-propanol	110-112°(4.3 mm.)	1.5270	3580, 3480 cm. ⁻¹	122° (13 mm.)(54)
2- <i>p</i> -Nitrophenyl-2-propanol		1.5530	3618, 3608 cm. ⁻¹ ^a	n_D^{19} 1.5552 (55)
3-Phenyl-3-pentanol	64-66°(1.2 mm.)	1.5141	3595 cm. ⁻¹	b.p. 109°(15 mm.) n_D^{20} 1.5165 (56)

(a) in CCl₄.

2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone. In a similar manner, 2,6-dimethylphenyl sulfones were prepared from 2-p-tolyl-2-propanol and 2-p-methoxyphenyl-2-propanol. Treatment of p-toluene-sulfinic acid in formic acid with 2-phenyl-2-propanol and 2-p-methoxyphenyl-2-propanol respectively, gave rise to the corresponding sulfones. Attempts to prepare 2-p-nitrophenyl-2-propyl 2,6-dimethylphenyl sulfone were unsuccessful. Longer reaction times, or reaction at elevated temperatures in the presence and absence of mineral acids yielded only 2,6-dimethylphenyl 2,6-dimethylbenzene thiolsulfonate.

TABLE XV

SUMMARY OF THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME 2-ARYL-2-PROPANOLS (CARBON DISULFIDE)

Compound	$\tau^{a,b}$		
	Ar-H	gem-dimethyl-H	Hydroxyl
2-Phenyl-2-propanol	3.0 (m)	8.65(s)	6.75(s)
2- <u>p</u> -Bromophenyl-2-propanol	3.0 (m)	8.65(s)	6.75(s)
2- <u>p</u> -Tolyl-2-propanol	3.0(q)	8.65(s)	6.75(s) 7.80(s) p-methyl
2- <u>p</u> -Methoxyphenyl-2-propanol ^c	3.1(m)	8.65(s)	7.21(s) 6.35(s) p-methoxy
2- <u>p</u> -Nitrophenyl-2-propanol	2.4(m)	8.55(s)	8.63(s)

^aChemical shifts are recorded in p.p.m. on the τ scale.

^bWhere s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

^cIn carbon tetrachloride.

All of the arenesulfinate esters were prepared by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethyl-

benzenesulfinate (Chapter I, page 14). The physical properties of the arenesulfinate esters and sulfones are listed in Table XIX, while the summary of their n.m.r. spectra appears in Table XX.

When a sample of 2-p-methoxyphenyl-2-propanol (which according to its n.m.r. spectrum contained ca. 15% of an impurity, possibly methoxybenzene) was treated with anhydrous hydrogen bromide in methylene chloride solution, after purification 2-p-methoxyphenyl-2-propyl bromide was isolated. Volhard titration gave a molecular weight of 266 which corresponds to 85.9% purity based on a calculated molecular weight of 229.1. The n.m.r. spectrum (carbon tetrachloride) of the material showed a multiplet at 2.95 τ and singlets at 6.38 and 7.92 τ in the ratio of 4.2:3.6:6.0. The multiplet at low field is due to the four aromatic protons, the singlet at high field due to the six methyl protons, while the remaining singlet is assigned to the p-methoxy group. Since neither in the infrared nor in the n.m.r. spectra is there a signal due to a hydroxyl group, the slight excess of aromatic and p-methoxy protons may be ascribed to an impurity which is relatively inert under the reaction conditions, possibly methoxybenzene.

Reaction of the bromide thus obtained with sodium azide in aqueous acetone, gave rise to a mixture containing 2-p-methoxyphenyl-2-propyl azide, olefin and alcohol. Distillation at reduced pressure removed most of the 2-p-methoxyphenylpropene. When the residue from distillation was chromatographed on alumina the required 2-p-methoxyphenyl-2-propyl azide was isolated. The infrared spectrum (carbon tetrachloride) of the material showed intense absorption at 2100 cm^{-1} , characteristic of azides (35), and no absorption in the vicinity of 875

TABLE XVI

PHYSICAL PROPERTIES OF THE OLEFINS AND ETHYL ETHERS.

Compound	b.p.	n_D^{25}	Identifying infra-red band, (CCl ₄)	Reported physical properties, reference
2-Phenylpropene	50-52°(12 mm.)	1.5354	895 cm. ⁻¹ a	b.p. 54-55°(15 mm.) n_D^{18} 1.5384 (57)
2-Phenyl-2-propyl ethyl ether	70-72°(8 mm.)	1.4915	1270 cm. ⁻¹	b.p. 48-49.5°(2.5 mm.) n_D^{22} 1.491 (58)
2-p-Bromophenyl-propene	64-66°(2.1 mm.)	1.5798	890 cm. ⁻¹	b.p. 110°(11 mm.) n_D^{20} 1.5835 (59) b.p. 58-60°(1.8 mm.) n_D^{27} 1.5778 (60)
2-p-Bromophenyl-2-propyl ethyl ether	100-102°(3.5 mm.)	1.5278	1245 cm. ⁻¹	
2-p-Tolylpropene	57-58°(5 mm.)	1.5331	890 cm. ⁻¹	b.p. 59°(5 mm.) n_D^{25} 1.5350 (61)
2-p-Tolyl-2-propyl ethyl ether	71-72°(3.5 mm.)	1.4895	1250 cm. ⁻¹	
2-p-Methoxyphenyl-propene	72-74°(6 mm.)	m.p. 31-33°	875 cm. ⁻¹ b	b.p. 63-63.5°(.5 mm.) m.p. 34° (62)
2-p-Methoxyphenyl-2-propyl ethyl ether		1.5017	1240 cm. ⁻¹	

(a) neat (b) in CS₂

TABLE XVII

SUMMARY OF THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF OLEFINS (CARBON TETRACHLORIDE)

Compound	τ^a		
	Ar -H	Olefinic-H	Methyl-H
2-Phenylpropene ^b	2.7(m)	4.76, 5.00(m)	8.00(d)
2- <u>p</u> -Bromophenyl-propene	2.7(m)	4.70, 4.95(m)	7.90(d)
2- <u>p</u> -Tolylpropene	2.9(m)	4.75, 5.10(m)	7.95(d) 7.75(s) <u>p</u> -methyl
2- <u>p</u> -Methoxyphenyl-propene	3.0(m)	4.80, 5.10(m)	7.95(d) 6.35(s) <u>p</u> -methoxy

^aChemical shifts are recorded in p.p.m. on the τ scale.

^bNeat.

cm.⁻¹ due to olefin. The n.m.r. spectrum (carbon tetrachloride) exhibited a multiplet at 3.0 τ and two singlets at 6.32 and 8.48 τ in the ratio of 4:3:6. These signals are assigned to the four aromatic, three methoxy and six methyl protons respectively.

Kinetics

2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate

2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate was allowed to react in 80% dioxane at 90° and in anhydrous ethanol at 70° and 90° in the presence of added 2,6-lutidine. Sample rate runs are given in Tables LXXIV, and LXXV, while a summary of the rates measured appears in Table XXI.

TABLE XVIII
SUMMARY OF THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF ETHYL ETHERS (CARBON TETRACHLORIDE)

Compound	\overline{J} (a)		
	Aromatic H	gem-dimethyl H Ether CH ₂	Ether CH ₃
2-Phenyl-2-propyl ethyl ether	2.70 (m)	8.55 (s)	6.85 (q) 8.90 (t)
2-p-Bromophenyl-2-propyl ethyl ether	2.65 (m)	8.55 (s)	6.85 (q) 8.90 (t)
2-p-Tolyl-2-propyl ethyl ether	2.85 (m)	8.55 (s)	6.85 (q) 8.90 (t); 7.70 (s) p-methyl
2-p-Methoxyphenyl-2-propyl ethyl ether	3.00 (m)	8.58 (s)	6.88 (q) 8.92 (t); 6.32 (s) p-methoxyl

(a) Chemical shifts are recorded in p.p.m. on the \overline{J} scale.

TABLE XIX

PHYSICAL PROPERTIES OF SULFINATE ESTERS AND SULFONES

Compound	Melting Point, °C	Identifying infra-red band, (cm. ⁻¹) (CS ₂)
2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate	82.5-83.0	1130
2-Phenyl-2-propyl 2,6-dimethylphenyl sulfone	152.5-153.0	1308 ^(a)
2-Phenyl-2-propyl 4-methylphenyl sulfone	146.5-147.2	1310 ^(a, b)
2- <u>p</u> -Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate	85.5-86.5	1125
2- <u>p</u> -Bromophenyl-2-propyl 2,6-dimethylphenyl sulfone	148.7-149.0	1308
2- <u>p</u> -Tolyl-2-propyl 2,6-dimethylbenzenesulfinate	51.5-52.0	1130
2- <u>p</u> -Tolyl-2-propyl 2,6-dimethylphenyl sulfone	139.5-140.0	1308
2- <u>p</u> -Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate	57.0-58.0	1125
2- <u>p</u> -Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone	107.5-108.0	1305, 660
2- <u>p</u> -Methoxyphenyl-2-propyl 4-methylphenyl sulfone	120.0-121.0	1302
2- <u>p</u> -Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate	103.5-104.0	1125
Ethyl 2,6-dimethylbenzenesulfinate	48.5-49.5	1145 ^(c)
Isopropyl 2,6-dimethylbenzenesulfinate		1145
Benzyl 2,6-dimethylbenzenesulfinate	43.0-44.0	1135
3-Phenyl-3-pentyl 2,6-dimethylbenzenesulfinate	68.0-69.5	1135

(a) in CCl₄ (b) Reported m.p. 144-145° (23) (c) Reported m.p. 47.3-48.6° (16)

TABLE XX

SUMMARY OF THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF SULFINATE ESTERS AND SULFONES (CARBON DISULFIDE)

Compound	τ (a)	
	Ar-H	Ar(CH ₃) ₂ C-(CH ₃) ₂
2-Phenyl-2-propyl 2,6-dimethyl-benzenesulfinate	2.90 (m)	7.58 (s) 8.18, 8.35 (s)
2-Phenyl-2-propyl 2,6-dimethyl-phenyl sulfone	2.80 (m)	7.92 (s) 8.30 (s)
2-Phenyl-2-propyl 4-methyl-phenyl sulfone	2.90 (d)	7.66 (s) 8.35 (s)
2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate	2.90 (m)	7.58 (s) 8.18, 8.35 (s)
2-p-Bromophenyl-2-propyl 2,6-dimethylphenyl sulfone	2.80 (m)	7.85 (s) 8.30 (s)
2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate	2.90 (m)	7.55 (s) 8.18, 8.35 (s) p-CH ₃ 7.71 (s)
2-p-Tolyl-2-propyl 2,6-dimethylphenyl sulfone	3.10 (m)	7.92 (s) 8.30 (s) p-CH ₃ 7.71 (s)
2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate	(b)	7.58 (s) 8.18, 8.35 (s) p-OCH ₃ 6.32 (s)

continued.

TABLE XX continued.

Compound	$\bar{\nu}$ (a)		
	Ar-H	Ar(CH ₃) ₂	C-(CH ₃) ₂
2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone	3.10 (m)	7.90 (s)	8.35 (s) p-OCH ₃ 6.30 (s)
2-p-Methoxyphenyl-2-propyl 4-methylphenyl sulfone	2.90 (m)	7.65 (s)	8.38 (s) p-OCH ₃ 6.28 (s)
2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate (c)	2.90 (m)	7.42 (s)	8.03, 8.14 (s)
Ethyl 2,6-dimethylbenzenesulfinate (d)	3.00 (m)	7.45 (s)	CH ₂ -5.98 (q) CH ₃ - 8.70 (t)
Isopropyl 2,6-dimethylbenzenesulfinate (d)	3.00 (m)	7.40 (s)	8.62, 8.74 (d) CH-5.50 (sept)
3-Phenyl-3-pentyl 2,6-dimethylbenzenesulfinate	2.80 (m)	7.48 (s)	CH ₂ -7.85 (m) CH ₃ - 9.30 (m)
Benzyl 2,6-dimethylbenzenesulfinate	2.85 (m)	7.52 (s)	CH ₂ -5.11 (s)

(a) Chemical shifts are recorded in p.p.m. on the $\bar{\nu}$ scale. (b) in the presence of a small amount of pyridine (c) in CCl₃ (d) in CCl₄

It is apparent from the control run (Table LXXVI), that considerable amount of acid is produced in the decomposition of the solvent, 80% dioxane at 90°. In forty hours, the time corresponding to ten half-lives of 2-p-bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate in 80% dioxane at 90°, the titer of a solution of 80% dioxane containing 2,6-lutidine and 2,6-dimethylbenzenesulfinic acid changes from 2.11 to 2.42 ml. The development of acid by aqueous dioxane solution at elevated temperatures has been noted earlier (page 35) as well as by other workers (41,42). When appropriate corrections are incorporated into the sample rate run II-243, Table LXXV, fairly good correlation between rates measured by titrimetry and infrared spectrophotometry is obtained. However, the corrected infinity titers correspond to 97.5% solvolysis and from the rates measured by infrared spectrophotometry 14.7% of 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone is formed. In effect, one is accounting for 112% of starting material. It is most likely that the corrections applied to the acid titers are not sufficiently large. The generation of acid from decomposition of the solvent is likely to be oxygen sensitive (41,42). Since no precautions were taken to exclude oxygen from the ampoules, the amount of oxygen is variable and thus the corrections may not be accurate.

In anhydrous ethanol at 70 and 90° good first-order rates were obtained. As shown in Table XXI (Run II-222,223; II-229,230), the rate constants measured by titrimetry and infrared spectrophotometry do not agree within the experimental errors indicated. Neither is there agreement between duplicate rates measured by infrared spectrophotometry. Compare Runs II-223, 230 and 238 at 90° and II-232 and II-240 at 70° in

TABLE XXI

SUMMARY ON REACTION OF 2-p-BROMOPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN VARIOUS SOLVENTS IN THE PRESENCE OF 2,6-LUTIDINE.

Run No.	Solvent	Temp. °C	Ester 10 ² M	Base 10 ² M(a)	10 ⁵ k, sec. ⁻¹	F _{solv.}	F _{rear.}
II-222	Anhyd. EtOH	90	2.08	4.68	7.45 ± .22	ca. .90	
II-223	Anhyd. EtOH	90	2.08	4.68	6.45 ± .11		.101
II-229	Anhyd. EtOH	90	2.08	4.50	7.74 ± .18	.907	
II-230	Anhyd. EtOH	90	2.08	4.50	6.57 ± .10		.100
II-237	Anhyd. EtOH	90	2.08	4.48	7.38 ± .29	.905	
II-238	Anhyd. EtOH	90	2.08	4.48	7.05 ± .38		.087
II-231	Anhyd. EtOH	70	2.08	4.50	1.032 ± .036	.905	
II-232	Anhyd. EtOH	70	2.08	4.50	.947 ± .021		.090
II-239	Anhyd. EtOH	70	2.08	4.48	1.042 ± .043	.904	
II-240	Anhyd. EtOH	70	2.08	4.48	1.034 ± .034		.089
II-224	80% Diox.	90	2.07	4.74	5.08 ± .11	.971	
II-225	80% Diox.	90	2.07	4.74	4.97 ± .11		.148
II-243	80% Diox.	90	2.09	4.76	5.09 ± .11	.980	
II-244	80% Diox.	90	2.09	4.76	4.95 ± .23		.147

(a) 2,6-Lutidine

anhydrous ethanol. Since rates, measured by both titrimetry and infrared spectrophotometry, measure the rate of arenesulfinate ester disappearance, they should coincide within experimental error. It is likely that the actual experimental errors in this case are greater than given by the average deviations from the mean values of the rate constants listed. The rate constants given are within ten per cent of one another and this may be a better estimate of the errors. Approximately 90% solvolysis and 9% rearrangement to 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone was observed in anhydrous ethanol, and the ratio is unaffected by the changes in the temperature at which the reaction is carried out. Ethanolysis at 90° is seven times faster than at 70°. As shown in Table XL, the titer of 2,6-dimethylbenzenesulfinic acid is stable under the latter conditions.

To determine the relationship between optical density and concentration for the sulfone, the same procedure was followed as for 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, described in Chapter I, page 19. In Figure X and Table XXII, it is shown that 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone adheres to the Lambert-Beer law up to .005 M concentration.

2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate

The reaction of 2-p-tolyl-2-propyl 2,6-dimethylbenzenesulfinate was carried out in 80% dioxane at 70° and in anhydrous ethanol at 70 and 90° in the presence of added 2,6-lutidine. Sample rate runs are given in Tables LXXVII, LXXVIII and LXXIX, while a summary of the rates measured appears in Table XXIII.

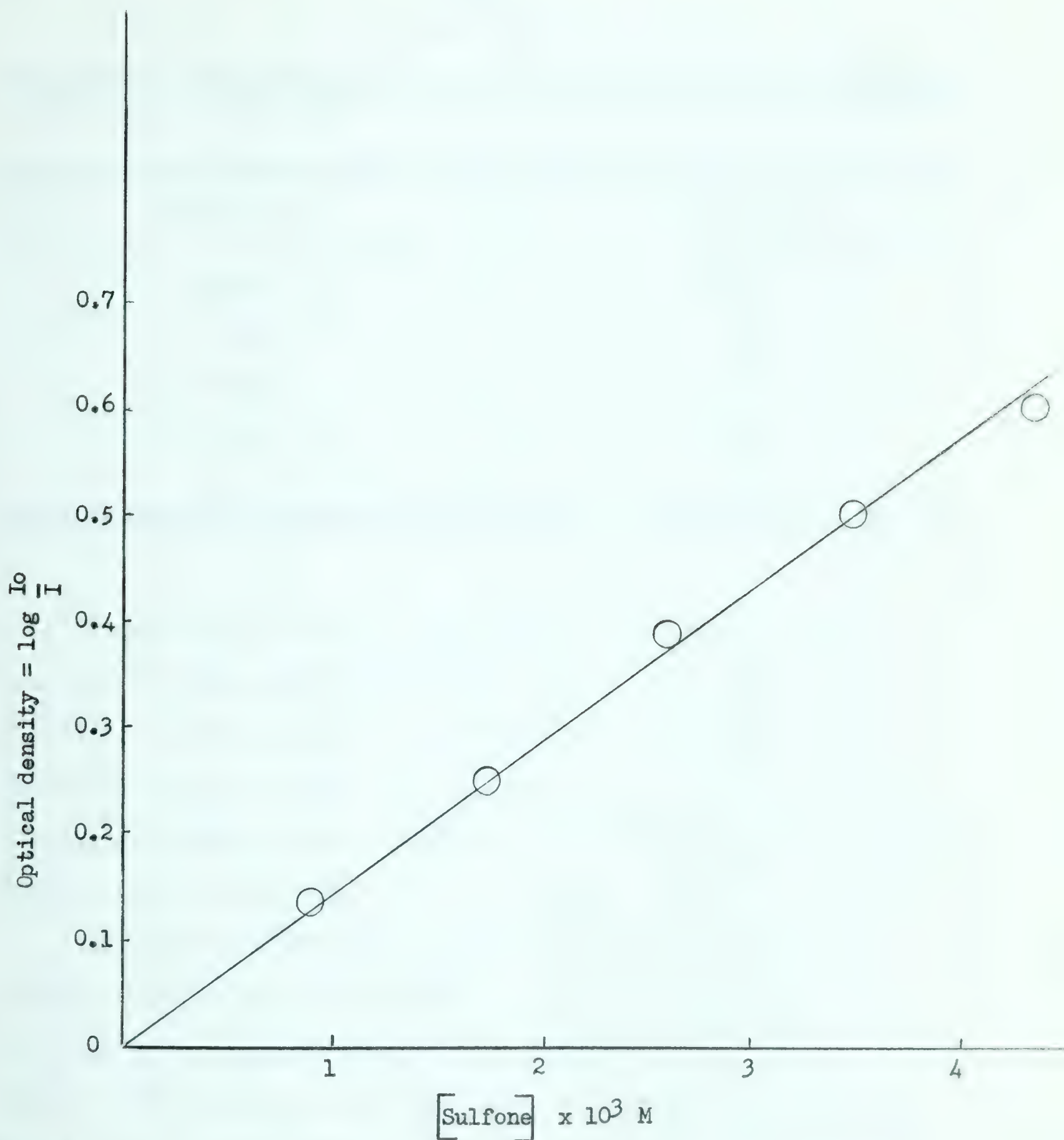


FIGURE X

Relationship between optical density and concentration for 2-p-Bromophenyl-
-2-propyl 2,6-dimethylphenyl sulfone in carbon tetrachloride at 1310 cm.⁻¹.

TABLE XXII

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR 2-p-BROMOPHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE (CARBON TETRACHLORIDE AT 1310 CM.⁻¹)

Sulfone, M	I_0/I	$\log I_0/I$
.00431	4.036	.60595
.00344	3.209	.50637
.00258	2.458	.39058
.00172	1.764	.24650
.00086	1.363	.13450

In anhydrous ethanol ca. 86% solvolysis and 13% rearrangement takes place as measured by infinity titers and sulfone concentrations. Addition of tetrabutylammonium 2,6-dimethylbenzenesulfinate has no appreciable effect on either the rate of reaction or on the ratio of solvolysis to rearrangement. (Compare Runs II-167,168 and III-23.). The reaction is 3.8 times faster at 90° in anhydrous ethanol than at 70°.

In 80% dioxane the ratio of solvolysis to rearrangement is slightly altered, from that observed in anhydrous ethanol, ca. 20% 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone was formed. It is apparent from control runs carried out on the stability of 2,6-dimethylbenzenesulfinic acid in 80% dioxane at 90°, that small amounts of acid are produced from decomposition of the solvent. It is probable that this phenomenon takes place at 70° as well, to a lesser extent, and is responsible for the sum of $F_{\text{solv.}}$ plus $F_{\text{rear.}}$ exceeding unity (1.036). Since any corrections to be applied would be quite small, the rate

TABLE XXIII

SUMMARY ON REACTION OF 2-p-TOLYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN VARIOUS SOLVENTS IN THE PRESENCE OF ADDED 2,6-LUTIDINE.

Run No.	Temp. °C	Solvent	Ester 10 ⁻² M	Base ^(a) 10 ⁻² M	10 ⁴ k, sec. ⁻¹	F _{solv.}	F _{rear.}
II-175	70	80% Diox.	2.14	4.57	7.04 ± .19	.836	
II-176	70	80% Diox.	2.14	4.57	7.21 ± .27		.200
II-167	70	Anhyd. EtOH	2.13	4.42	9.85 ± .25	.892	
II-168	70	Anhyd. EtOH	2.13	4.42	9.81 ± .28		.130
III-23 ^(b)	70	Anhyd. EtOH	2.29	4.46	9.78 ± .18	.856	.140
III-21	90	Anhyd. EtOH	2.18	4.48	37.0 ± .20	.840	.133

(a) 2,6-Lutidine. (b) Tetrabutylammonium 2,6-dimethylbenzenesulfinate (.0560 M) added.

constants listed in Table XXIII have not been corrected.

To determine the relationship between optical density and concentration for the sulfone, the same procedure was used as for 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone. As shown in Figure XI and Table XXIV, 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone adheres to the Lambert-Beer law up to .005 M concentration.

TABLE XXIV

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR 2-p-TOLYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE (CARBON TETRACHLORIDE AT 1308 CM.⁻¹)

Sulfone, M	I ₀ /I	log I ₀ /I
.00474	4.921	.69205
.00379	3.975	.59934
.00284	2.609	.41647
.00189	1.986	.29588
.00095	1.481	.17050

2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate

Reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate was carried out in anhydrous acetic acid at 90° with added sodium acetate. Due to the unavailability of a convenient titrimetric method to follow solvolysis in acetic acid, and the lack of formation of significant amounts of 2-p-nitrophenyl-2-propyl 2,6-dimethylphenyl sulfone, it was necessary to use n.m.r. to measure the disappearance of this ester. The rate of ester disappearance was followed by

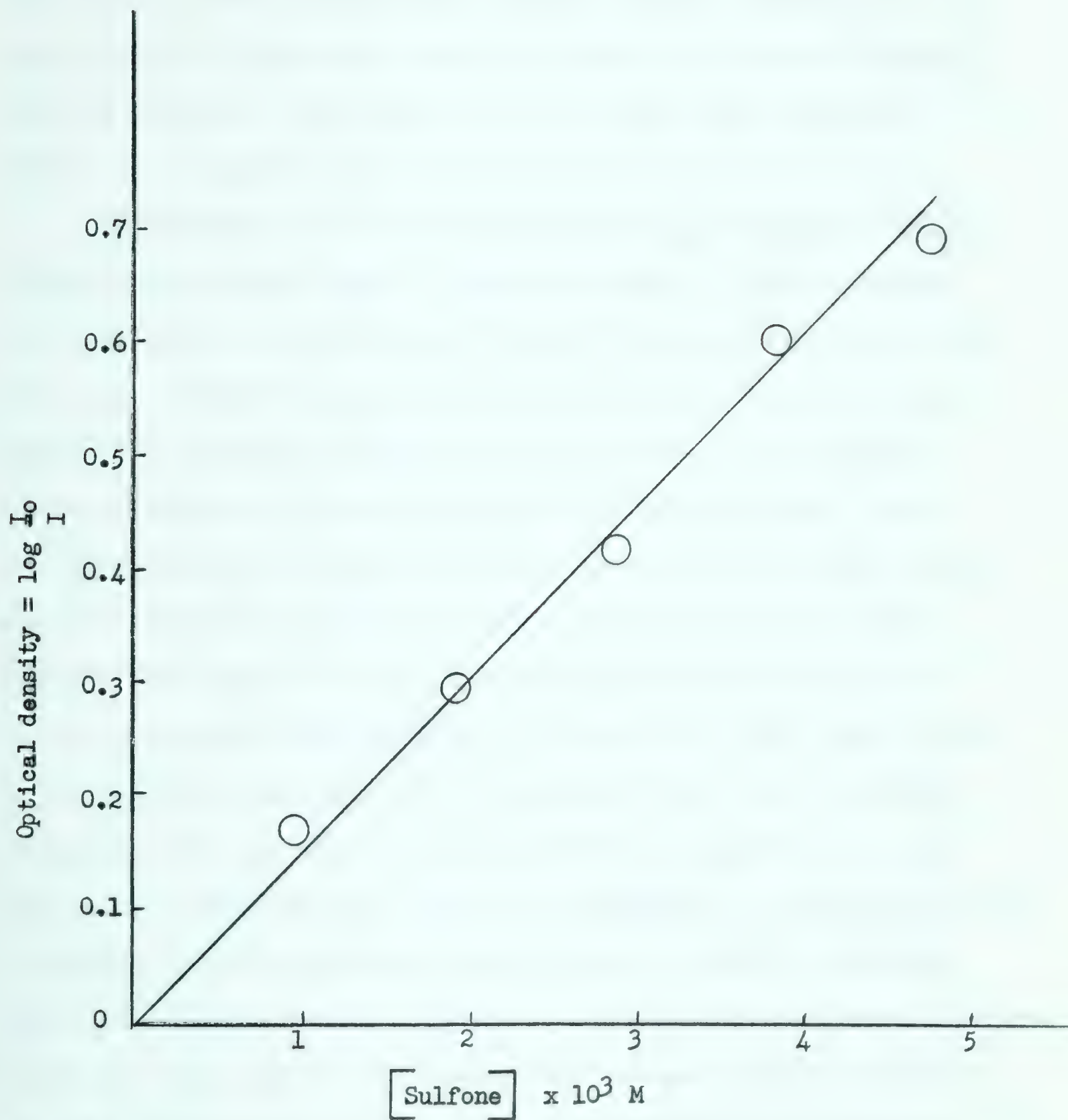


FIGURE XI

Relationship between optical density and concentration for 2-p-Tolyl-2-propyl 2,6-dimethylphenyl sulfone in carbon tetrachloride at 1308 cm^{-1} .

measurement of the band due to the two methyl groups ortho to the sulfur atom of the arenesulfinate group at 7.40 τ in chloroform. From the ratio of the integrated areas of the sample to internal standard, ethylene carbonate, the first-order rate constant was calculated. Results of a sample rate are given in Table LXXX.

Measurement of the rate of reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90°, with added 2,6-lutidine, is complicated by a number of factors. The solubility of the ester in anhydrous ethanol is lower than any of the other esters, the maximum concentration appears to be ca. .010-.012 M. The acid titers obtained were rather erratic as shown in Table LXXXI. Due to the low solubility of the arenesulfinate ester in pentane, ethyl ether was substituted for pentane in the extraction procedure, and 25 ml. aliquots were taken. The rate of ester disappearance was measured by n.m.r. by following the reduction of the signal at 7.40 τ which is due to the aromatic methyl groups of the arenesulfinate ester. However, measurement of the area of this band at 60 Mc. is complicated by the appearance of a new band at 7.32 τ . The appearance of a singlet at 7.32 τ along with a triplet at 8.65 τ and a quartet at 5.82 τ is consistent with the assignment of these signals to ethyl 2,6-dimethylbenzenesulfinate. At 100 Mc., the signals at 7.32 and 7.40 τ are well resolved and from the integrated areas the rate of ester disappearance was calculated.

At the start of the reaction only 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate and no ethyl 2,6-dimethylbenzenesulfinate is present. During the reaction, the concentration of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate decreased, while the concentration

of ethyl 2,6-dimethylbenzenesulfinate increased. The ratio of ethyl 2,6-dimethylbenzenesulfinate formed to 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate reacted, "F*", is highly sensitive to small changes in the concentration of the former, especially near the beginning of the reaction. Thus the value of "F*" at the two initial points in Table LXXXII at 28 and 72 hours, respectively, is subject to a relatively large error. Inspection shows that the value of "F*" is approximately constant as expected, if ethyl 2,6-dimethylbenzenesulfinate is a primary product of the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate. Thus about 27% ethyl 2,6-dimethylbenzenesulfinate is formed during the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° in the presence of 2,6-lutidine. From the value of the observed first-order rate constant, $k_{\text{ethyl ester}}$ formation was calculated to be $3.5 \times 10^{-7} \text{ sec.}^{-1}$.

It should be noted that the n.m.r. spectrum of the material which was heated for 259 hours in the 90° constant temperature bath is more complicated than indicated earlier. From 5.50 to 7.00 τ three sets of quartets are observed, while from 8.50 to 9.00 τ three sets of triplets are noted. Since 2-p-nitrophenyl-2-propyl ethyl ether has not been synthesized, the assignment of the n.m.r. signals must be tentative. Provisionally, the above signals may be assigned to ethyl 2,6-dimethylbenzenesulfinate, 2-p-nitrophenyl-2-propyl ethyl ether and residual ethyl ether (from the extraction). In Table LXXXII a sample rate for 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate disappearance, and ethyl 2,6-dimethylbenzenesulfinate appearance is given.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate

The reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate was carried out in anhydrous ethanol at 0 and 25° in the presence of added 2,6-lutidine. A sample titrimetric rate (Run II-250) is given in Table LXXXIII. The precision obtained is considerably lower than recorded in any of the previous rate runs.

The standard kinetic procedure of delivering an aliquot into pentane-water, followed by extraction did not effectively quench the reaction. This could be due to appreciable solubility of the arenesulfinate ester in water, or solvolysis during the extraction procedure. When samples of the ester were dissolved in anhydrous dioxane, the dioxane solution added to pentane-water and extracted, titers of .60 and .72 ml. were obtained. These values correspond to 26 and 31% of the theoretical infinity titers. Most of the titer must arise through hydrolysis of the arenesulfinate ester, since it is known from the infrared and n.m.r. spectra that the compound is more than 94 per cent pure.

When other arenesulfates were subjected to the above procedure, the initial titers did not exceed more than four per cent of the theoretical infinity titer. From their infrared and n.m.r. spectra we estimate their purity to be higher than 98 per cent in each case.

We therefore turned our attention toward devising an alternate titrimetric procedure that would not involve an extraction procedure. Various concentrations of 2,6-dimethylbenzenesulfinic acid in the presence of 2,6-lutidine were prepared in anhydrous ethanol and titrated with sodium methoxide using p-naphtholbenzein as indicator. The

observed and calculated end points in all cases coincided within less than 0.5 per cent as shown in Table XXV.

Good first-order kinetics were obtained by the use of the above method of direct titration. In the reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 0° and 25° no "blanks" were taken. Due to the solvolysis of the arenesulfinate ester during extraction, the rate of sulfone appearance could not be measured by infrared spectrophotometry. The "infinity points" from the reaction after titration, were extracted by the regular method and the concentration of sulfone and azide, if any, were measured. 2-p-Methoxyphenyl-2-propyl ethyl ether, 2-p-methoxyphenyl-2-propyl azide, 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone as well as 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate have absorption bands at or near 1310 cm^{-1} , therefore this region cannot be used for quantitative determination of the sulfone. The amount of sulfone formed was measured in acetonitrile at 660 cm^{-1} where there is no interference in absorption from other products of the reaction. Sample reaction rates are given in Tables LXXXIV and LXXXV.

As shown in Figure XII and Table XXVI, a linear relationship has been found between optical density and concentration for 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone.

At both 0 and 25° in anhydrous ethanol about 80% solvolysis and 21% rearrangement to 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone was observed (Table XXVIII). The rate of reaction at 25° is twenty times faster than at 0°. Addition of tetrabutylammonium 2,6-dimethylbenzenesulfinate (Runs II-260 and III-34 in Table XXVIII) has no effect on

TABLE XXV

CONTROL TITRATION OF 2,6-DIMETHYLBENZENESULFINIC ACID IN ANHYDROUS ETHANOL WITH ADDED 2,6-LUTIDINE(.04518 M).

Indicator: Phenolphthalein. Base: NaOCH_3 (.03888 M). Aliquot: 5.046 ml.

Acid, (a) 10^2 M	Titers (ml.)	Average titer found (ml.)	Theoretical titer (ml.)
1.681	2.188, 2.198, 2.195	2.194	2.184
1.008	1.323, 1.339, 1.335	1.332	1.324
0.336	.451, .442, .446	.446	.436
Blank	.039, .027		

Indicator: p-Naphtholbenzein. Base: NaOCH_3 (.03888 M) .Aliquot:4.964ml.

Acid, (a) 10^2 M	Titers (ml.)	Average titer found (ml.)	Theoretical titer (ml.)
1.681	2.139, 2.142, 2.143	2.141	2.145
0.672	.850, .857, .860	.858	.858
0.168	.212, .214, .222, .215	.216	.215
Blank	.005, .006		

(a) 2,6-Dimethylbenzenesulfinic acid.

either the rate of reaction or on the product distribution. Addition of lithium perchlorate shows a small salt effect with a "b" value of 6.8 (Runs II-261 and II-266). In the presence of .075 M lithium perchlorate the yield of sulfone is reduced from 21% to 16.3%. A sample rate run in the presence of lithium perchlorate is given in Table LXXXVII.

Addition of tetrabutylammonium 4-methylbenzenesulfinate has no effect on the rate of reaction. (Table XXVIII, Run II-279). The composition of the rearrangement product under these conditions is given in the next section, and a sample rate is shown in Table LXXXVIII.

A number of runs were carried out in the presence of added tetrabutylammonium azide. The presence of high concentrations of azide ion, tended to reduce the sharpness of the end point in the titrations. A similar observation has been earlier noted in the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in the presence of high 2,6-lutidine concentrations. The 2-p-methoxyphenyl-2-propyl azide formed was measured at 2100 cm^{-1} (acetonitrile). The relationship between optical density and concentration for this compound is shown in Figure XIII and Table XXVII. As illustrated in Figure XIII, the relationship is linear only up to .006 M concentration. A sample rate run in the presence of added tetrabutylammonium azide is given in Table LXXXIX. The addition of tetrabutylammonium azide has no effect on the rate of reaction, but brings about considerable changes in product distribution (see Table XXVIII, Runs III-30, III-31 and III-35). It is apparent from Table XXIX that the formation of both solvolysis and rearrangement products is reduced roughly to the same extent by the addition of azide ion. In contrast to the unsubstituted ester there is no doubt in this

TABLE XXVI

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR 2-p-METHOXY-PHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE (IN ACETONITRILE AT 660 CM.⁻¹)

Sulfone, Molar	$\frac{I_0}{I}$	$\log \frac{I_0}{I}$
0.00664	2.160	0.33445
.00531	1.891	.27669
.00398	1.629	.21192
.00332	1.489	.17289
.00266	1.380	.13988
.00133	1.162	.06521

TABLE XXVII

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR 2-p-METHOXY-PHENYL-2-PROPYL AZIDE (IN ACETONITRILE AT 2100 CM.⁻¹)

Azide, Molar	$\frac{I_0}{I}$	$\log \frac{I_0}{I}$
0.01253	12.371	1.0923
.01003	9.650	.98453
.00752	6.658	.82334
.00626	4.649	.66736
.00501	3.928	.59406
.00251	1.984	.29754

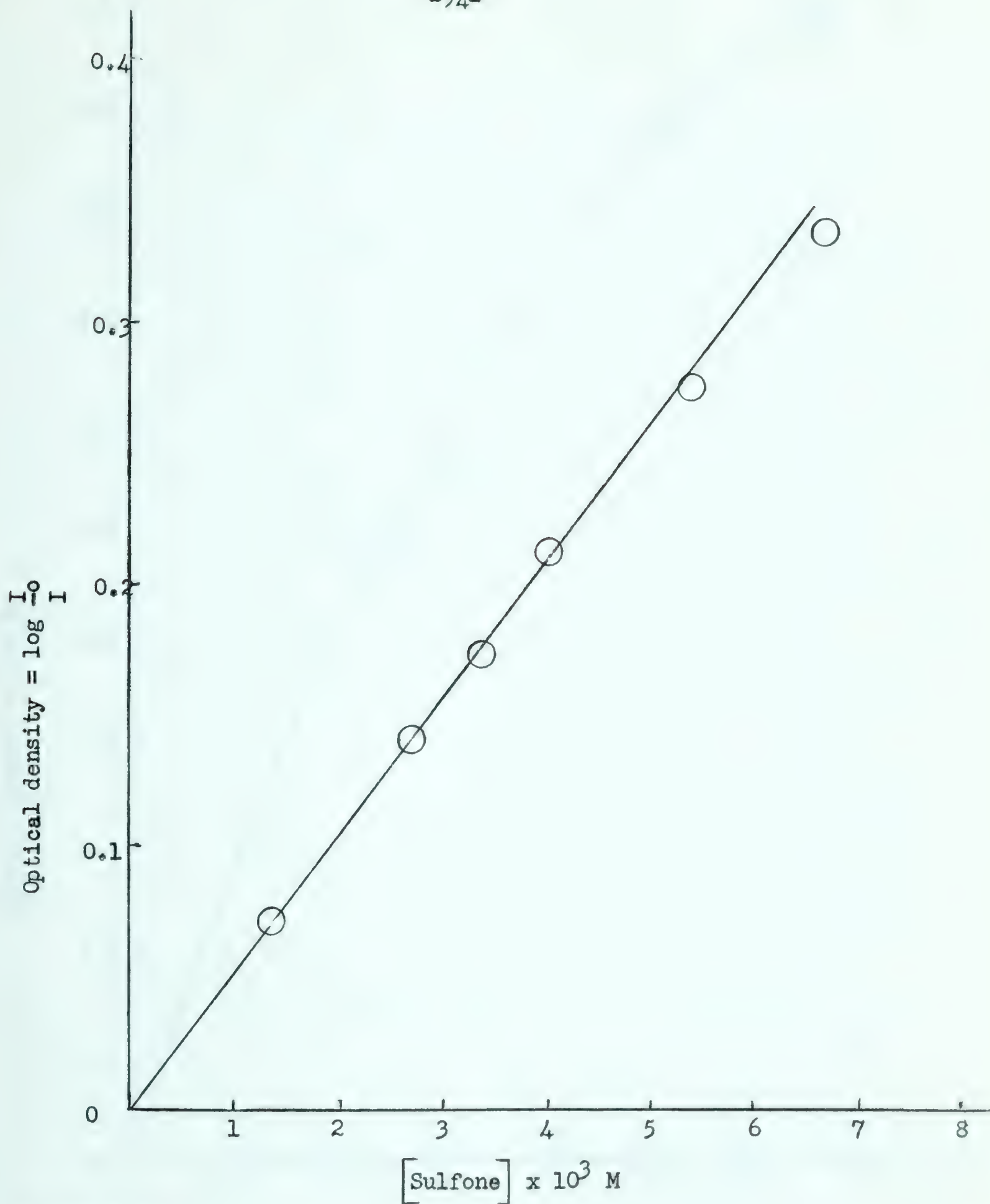


FIGURE XII

Relationship between optical density and concentration for 2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone in acetonitrile at 660 cm.⁻¹.

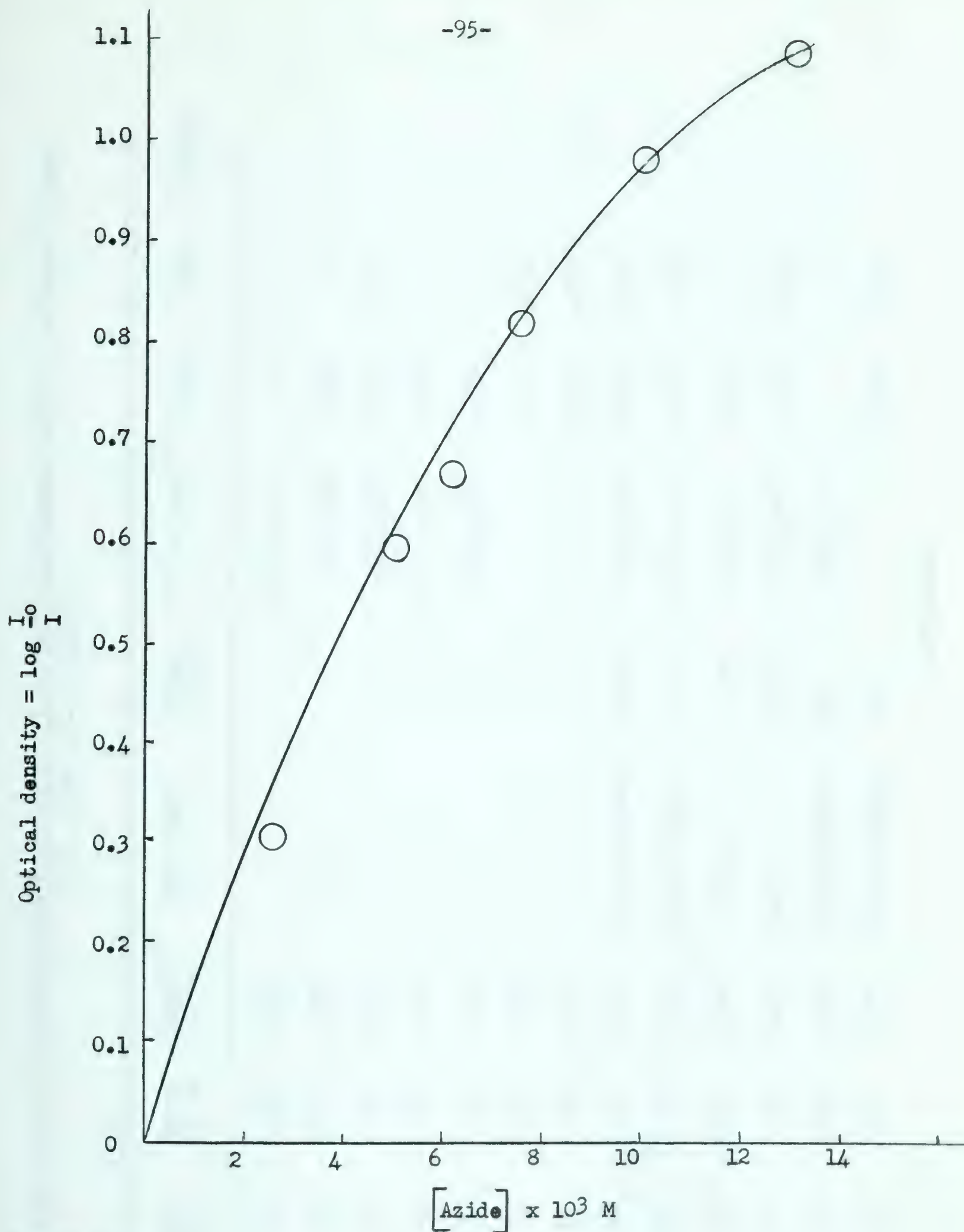


FIGURE XIII

Relationship between optical density and concentration for 2-p-Methoxyphenyl-2-propyl azide in acetonitrile at 2100 cm.^{-1} .

TABLE XXVIII

SUMMARY ON REACTION OF 2-*p*-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE IN ANHYDROUS ETHANOL
WITH ADDED 2,6-LUTIDINE.

Run No.	Temp. °C	Ester 10 ² M	Base (a) 10 ² M	Added Salt	Conc. 10 ² M	10 ³ k, sec. ⁻¹	F _{solv.}	F _{rear.}	F _{azide}
II-250 ^(b)	25	2.15	4.35			2.0 ± .6			
II-263	0	2.19	4.37			.108 ± .003	.815		
II-278	0	1.97	4.36			.104 ± .003	.811	.203	
II-259	25	2.17	4.33			2.11 ± .05	.816		
II-262	25	2.33	4.50			2.04 ± .05	.813		
III-28	25	2.24	4.80				.804	.210	
III-42	25	2.23	4.51				.772	.223	
II-260 ^(c)	25	2.26	4.61	Bu ₄ N C ₈ H ₉ SO ₂	3.40	2.07 ± .03	.808	.193	
III-34 ^(c)	25	2.26	4.55	Bu ₄ N C ₈ H ₉ SO ₂	3.34	2.03 ± .02	.809	.202	
II-261	25	2.22	4.66	LiClO ₄	3.69	2.53 ± .05	.817		
II-266	25	2.16	4.61	LiClO ₄	7.49	3.35 ± .05	.825	.163	
II-279 ^(d)	25	2.22	4.67	Bu ₄ N C ₇ H ₇ SO ₂	25.9	1.96 ± .09			
III-43 ^(d)	25	2.24	4.37	Bu ₄ N C ₇ H ₇ SO ₂	26.0		.730	.178	

continued.

TABLE XXVIII continued.

Run No.	Temp. °C	Ester 10 ² M	Base (a) 10 ² M	Added Salt	Conc. 10 ² M	10 ³ k, sec. ⁻¹	F _{solv.}	F _{rear.}	F _{azide}
II-267 ^(e)	25	2.52	4.63	Bu ₄ N N ₃	9.18	2.02 ± 0.03	.590		
III-30	25	2.37	4.85	Bu ₄ N N ₃	9.12		.600	.164	.258
II-268	25	2.26	4.42	Bu ₄ N N ₃	15.55	2.16 ± 0.05	.503		.368
III-31	25	2.28	4.90	Bu ₄ N N ₃	21.74		.475	.133	.444
III-35	25	2.32	4.46	Bu ₄ N N ₃	29.13	2.06 ± 0.06	.388	.114	.583
II-269	25	2.31	4.46	Bu ₄ N N ₃	33.07		.398		

- (a) 2,6-Lutidine
 (b) Kinetic Method A used.
 (c) Tetrabutylammonium 2,6-dimethylbenzenesulfinate
 (d) Tetrabutylammonium 4-methylbenzenesulfinate
 (e) Tetrabutylammonium azide

TABLE XXIX

THE EFFECT OF AZIDE ION ON REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENSULFINATE IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE

Run	Bu ₄ N N ₃ 10 ² , M	F _{solv.}	F _{rear.}	F _{azide}	Reduction in % solv. % rear.	
(a)	--	.811	.210			
III-30	9.12	.600	.164	.258	24.6	22.0
III-31	21.74	.475	.133	.444	41.4	37.0
III-35	29.13	.388	.114	.583	52.0	46.0

^aAverage of several determinations (Runs II-259, II-262, III-28).

case of the reduced amounts of sulfone formed.

An exchange experiment was carried out in the following manner. 2-p-Methoxyphenyl-2-propyl bromide (.03072 M) was treated for three minutes in anhydrous ethanol at 25° in the presence of tetrabutylammonium 2,6-dimethylbenzenesulfinate (.03130 M) and 2,6-lutidine (.1938 M). 2-Phenyl-2-propyl bromide under comparable conditions would be expected to have a half-life of ca. 3 minutes (Chapter I, page 34). If we allow a factor of 10³ for the effect of the additional methoxy group, the reaction would be expected to be completed in less than 20 seconds. Hence, 3 minutes represents complete reaction.

On solvolysis, 84.1 per cent of the theoretical amount of acid, and 82.3 per cent of the theoretical amount of bromide ion were produced. The values of 82.3 and 84.1 per cent are in fair agreement with the experimentally determined 85.9 per cent purity of the starting bromide.

Measurement of the percentage transmittance in acetonitrile at ca. 660 cm.^{-1} gives a maximum of 1.14% sulfone, which would correspond to 5.4% of the sulfone formed in the reaction of the arenesulfinate ester.

Product Runs

A series of standards consisting of various ratios of 2-p-bromophenylpropene, 2-p-bromophenyl-2-propyl ethyl ether and acetophenone (internal standard) were prepared and analyzed by gas chromatography. The area ratio of compound to internal standard was calculated and plotted against the mole ratio of component to internal standard. These results are given in Figure XIV and Table XXX.

A synthetic mixture consisting of 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone, 2-p-bromophenyl-2-propyl ethyl ether, 2-p-bromophenylpropene and 2,6-lutidine was prepared, dissolved in anhydrous ethanol and immersed in the 90° constant temperature bath for 33 hours (11 half-lives for the reaction of the corresponding arene-sulfinate ester). Subsequent treatment was exactly as described for the unsubstituted system, except in gas chromatography, the Perkin Elmer column K at 174° was used. The results obtained are listed in Table XXXI.

In product run III-5, .7713 g. (.00210 mole) of 2-p-bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate and .4785 g. (.00447 mole) of 2,6-lutidine were dissolved in 100 ml. of anhydrous ethanol and the solution was heated in the 90° constant temperature bath for 33 hours (11 half-lives for the reaction of the ester). Subsequent treatment was exactly as described in the control run above.

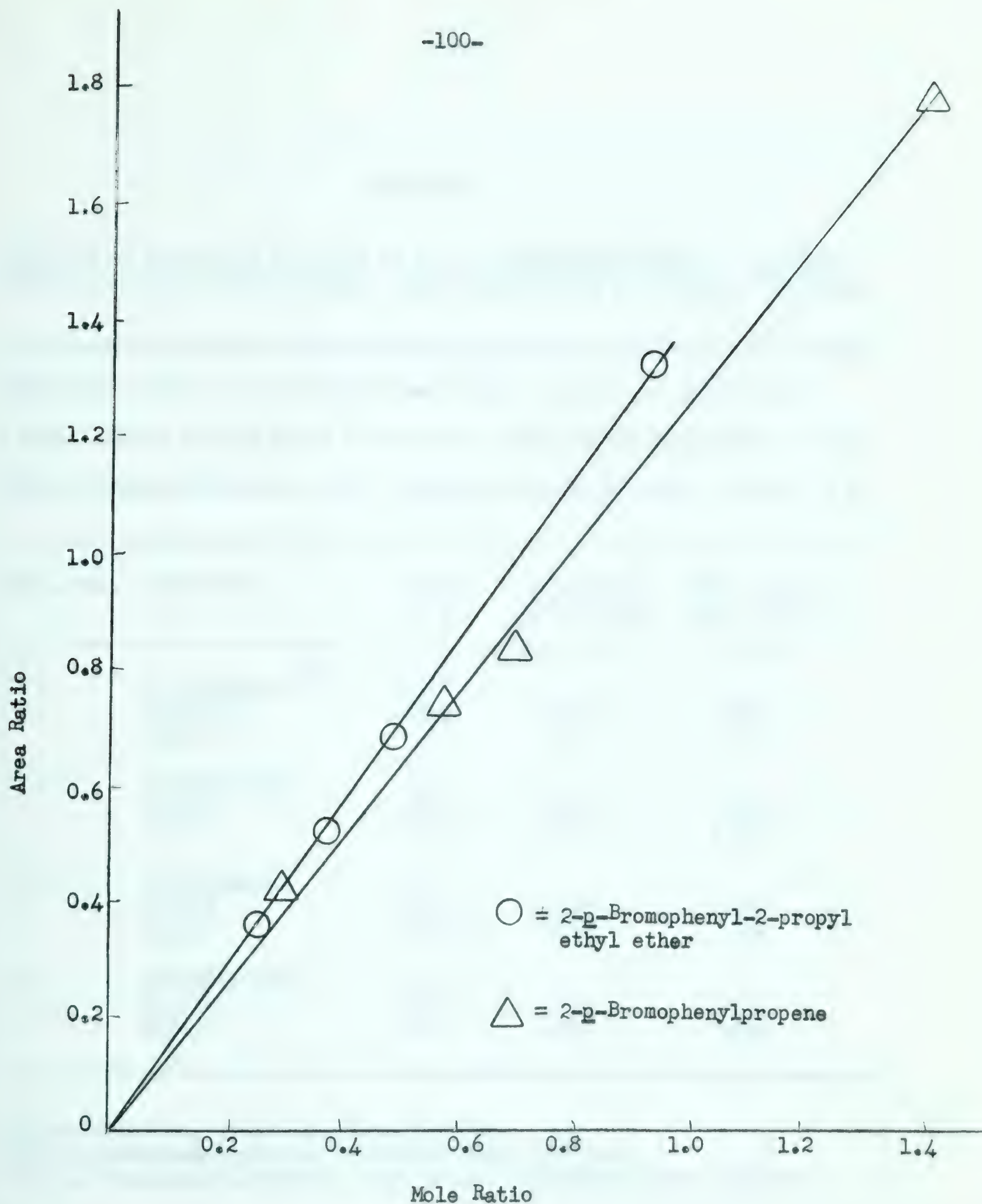


FIGURE XIV

Calibration curve for gas liquid chromatography of 2-p-bromophenyl-2-propyl ethyl ether and 2-p-bromophenylpropene, using acetophenone as internal standard.

TABLE XXX

ANALYSES OF SYNTHETIC MIXTURES OF 2-p-BROMOPHENYLPROPENE AND 2-p-BROMOPHENYL-2-PROPYL ETHYL ETHER, USING ACETOPHENONE AS INTERNAL STANDARD.

Operating Conditions of Perkin Elmer Vapor Fractometer Model 154 D:
2 Meter Column Perkin Elmer K (carbowax 1500); Column Temperature: 174°;
Column Pressure(Helium): 25/5.6 (gauge pressure); Detector Voltage: 8 V.

Sample No.	Components	Weight in g.	Calculated mole ratio.	Found average area ratio.
I	Acetophenone ^(a)	0.116		
	Olefin ^(b)	.112	0.587	0.744
	Ether ^(c)	.117	.497	.673
II	Acetophenone	.118		
	Olefin	.060	.309	.412
	Ether	.224	.938	1.317
III	Acetophenone	.112		
	Olefin	.260	1.415	1.778
	Ether	.060	.265	.360
IV	Acetophenone	.114		
	Olefin	.133	.711	.832
	Ether	.089	.385	.506

(a) Acetophenone, retention time: 590 sec.

(b) 2-p-Bromophenylpropene, retention time: 725 sec.

(c) 2-p-Bromophenyl-2-propyl ethyl ether, retention time: 1090 sec.

TABLE XXXI

CONTROL ISOLATION OF 2-p-BROMOPHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE
2-p-BROMOPHENYLPROPENE AND 2-p-BROMOPHENYL-2-PROPYL ETHYL ETHER IN ANHYD-
ROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (RUN III-1)

Compound	Weight in g.	Initial moles, 10 ³	Recovered moles, 10 ³	Per Cent Recovery
Sulfone	.0732	.199	.195 ^a	97.5
Olefin	.1700	.863	.815 ^b	94.4
Ether	.2291	.943	.898 ^b	95.3
2,6-Lutidine	.4860	4.535	--	

^aGravimetrically.

^bBy gas chromatography.

Analysis by gas chromatography showed the presence of 41.8% 2-p-bromophenylpropene and 48.7% 2-p-bromophenyl-2-propyl ethyl ether. The above percentage values are not corrected for the ca. 95% recovery in the control run III-1. The 64.5 mg. of 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone obtained corresponds to 8.4 per cent based on starting ester. The 90.5% solvolysis products and 8.4% sulfone compare well with the values of 90.6% and ca. 9% obtained in kinetic runs.

2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate

A series of standards consisting of various ratios of 2-p-tolylpropene, 2-p-tolyl-2-propyl ethyl ether and acetophenone (internal standard) were prepared and analyzed by gas chromatography as described for the corresponding p-bromo compounds. The results obtained are given

in Figure XV and Table XXXII.

A synthetic mixture consisting of 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone, 2-p-tolylpropene, 2-p-tolyl-2-propyl ethyl ether and 2,6-lutidine was prepared, dissolved in anhydrous ethanol and heated in the 90° constant temperature bath for 70 minutes (25 half-lives for the reaction of the corresponding arenesulfinate ester). Subsequent treatment was exactly as described for the unsubstituted system except in gas chromatography, the Perkin Elmer column K at 140° was used. The results obtained are listed in Table XXXIII.

In product run III-16, .6696 g. (.00221 mole) of 2-p-tolyl-2-propyl 2,6-dimethylbenzenesulfinate and .4740 g. (.00442 mole) of 2,6-lutidine were dissolved in 100 ml. of anhydrous ethanol and the solution was heated in the 90° constant temperature bath for 50 minutes (ca. 20 half-lives for the reaction of the ester). Subsequent treatment was exactly as described in the control run above.

Analysis by gas chromatography showed the presence of 30.3% 2-p-tolylpropene and 53.9% 2-p-tolyl-2-propyl ethyl ether. The 96.5 mg. of 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone isolated corresponds to 14.4 per cent based on starting ester. The 84.2% of solvolysis products and 14.4% sulfone compare well with the values of 86% and 13% obtained in the kinetic runs.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate

Preliminary gas chromatography on Perkin Elmer columns C, K and R showed that 2-p-methoxyphenyl-2-propyl ethyl ether could not be analyzed due to its decomposition. The n.m.r. spectrum of the material obtained on reaction of the arenesulfinate ester in ethanol, showed the presence of only ether and sulfone, no olefin. However, 2-p-methoxyphenyl-

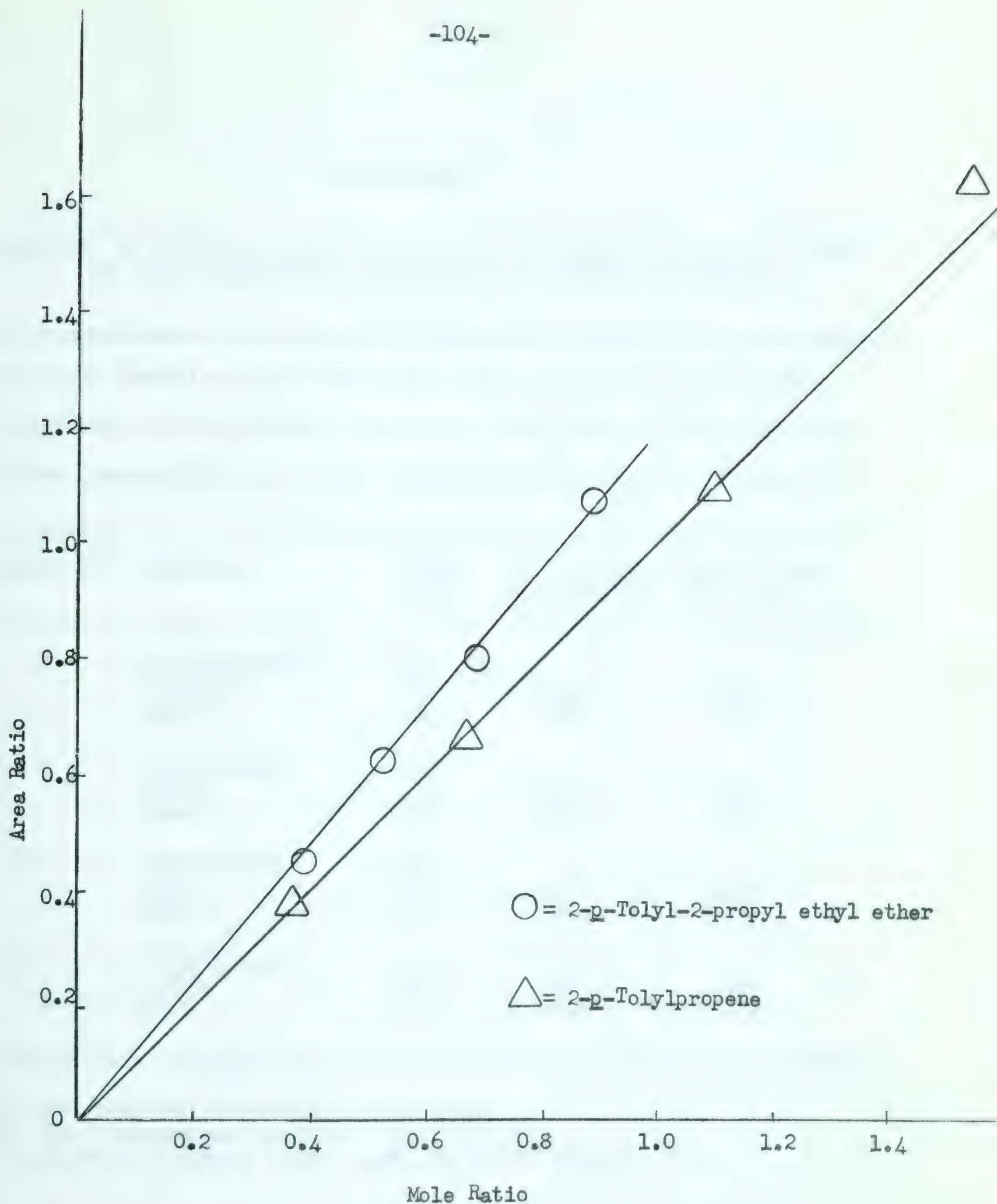


FIGURE XV

Calibration curve for gas liquid chromatography of 2-p-tolyl-2-propyl ethyl ether and 2-p-tolylpropene, using acetophenone as internal standard.

TABLE XXXII

ANALYSES OF SYNTHETIC MIXTURES OF 2-p-TOLYLPROPENE AND 2-p-TOLYL-2-PROPYL ETHYL ETHER, USING ACETOPHENONE AS INTERNAL STANDARD.

Operating Conditions of Perkin Elmer Vapor Fractometer Model 154 D:

2 Meter Column Perkin Elmer K (carbowax 1500); Column Temperature: 140°;

Column Pressure(Helium): 25/5.6 (gauge pressure); Detector Voltage: 8 V.

Sample No.	Components	Weight in g.	Calculated mole ratio.	Found average area ratio.
I	Acetophenone ^(a)	0.131		
	Olefin ^(b)	.095	0.659	0.662
	Ether ^(c)	.133	.684	.802
II	Acetophenone	.125		
	Olefin	.150	1.090	1.095
	Ether	.070	.377	.443
III	Acetophenone	.132		
	Olefin	.223	1.535	1.628
	Ether	.103	.526	.621
IV	Acetophenone	.123		
	Olefin	.049	.362	.379
	Ether	.162	.888	1.065

(a) Acetophenone, retention time: 1380 sec.

(b) 2-p-Tolylpropene, retention time: 520 sec.

(c) 2-p-Tolyl-2-propyl ethyl ether, retention time: 780 sec.

TABLE XXXIII

CONTROL ISOLATION OF 2-p-TOLYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE, 2-p-TOLYLPROPENE AND 2-p-TOLYL-2-PROPYL ETHYL ETHER IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (RUN III-13)

Compound	Weight in g.	Initial moles, 10 ³	Recovered moles, 10 ³	Per Cent Recovery
Sulfone	.0573	.189	.184 ^a	97.5
Olefin	.1566	1.186	1.153 ^b	97.2
Ether	.2012	1.130	1.115 ^b	98.7
2,6-Lutidine	.5101	4.760	--	

^a Gravimetrically. ^b By gas chromatography.

2-propyl ethyl ether, is partially lost, due to its volatility, during the removal of the pentane at the water pump. To avoid interference from the methyl and methylene groups of pentane in the n.m.r., all of the solvent must be removed prior to recording of the spectrum. However, if methylene chloride is used as solvent for the extraction, the n.m.r. spectrum can be recorded without interference from the methylene protons, thus there is no need for quantitative removal of this solvent.

In control run III-37, a synthetic mixture consisting of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone, 2-p-methoxyphenyl-2-propyl ethyl ether and 2,6-lutidine were dissolved in 50 ml. of anhydrous ethanol and the solution was kept in the 25° constant temperature bath for one hour (ca. 11 half-lives for the reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate). The solution was poured into methylene chloride-water and extracted in the usual manner. After drying, the solvent was removed

by slow distillation through two 9" Vigreux columns and a known amount of ethylene carbonate (internal standards) was added. The n.m.r. spectrum was recorded at 100 Mc., and from the ratio of areas obtained, the percentage of each compound recovered was calculated. From the results shown in Table XXXIV, it is apparent that this method may be successfully applied for product determinations.

TABLE XXXIV

CONTROL ISOLATION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLPHENYL SULFONE, 2-p-METHOXYPHENYL-2-PROPYL 4-METHYLPHENYL SULFONE AND 2-p-METHOXYPHENYL-2-PROPYL ETHYL ETHER IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE (RUN III-37)

Compound	Weight in g.	Initial moles, 10 ⁴	Recovered moles, 10 ⁴	Percentage recovery	n.m.r. signal τ measured at 100 Mc.
Sulfone I ^a	.0391	1.23	1.22	99	7.78
Sulfone II ^b	.0034	.111	.105	95	7.60
Ether ^c	.0912	4.70	4.31	92	8.55

^a2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone.

^b2-p-Methoxyphenyl-2-propyl 4-methylphenyl sulfone

^c2-p-Methoxyphenyl-2-propyl ethyl ether.

Accordingly in Run III-42, .3547 g. (.001114 mole) of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate and .2418 g. (.002256 mole) of 2,6-lutidine were weighed into a 50 ml. volumetric flask which was filled to the mark with anhydrous ethanol. The flask was placed into the 25° constant temperature bath for one hour (ca. 11 half-lives for the reaction of the ester). The same isolation procedure was used as in the

foregoing control experiment. The n.m.r. spectrum was recorded at both 60 and 100 Mc., and from the area ratios obtained, the percentages of 2-p-methoxyphenyl-2-propyl ethyl ether and 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone were calculated. The results obtained are given in Table XXXV. It should be noted that there is about 7 per cent difference between the percentages of the components analyzed on the A-60 and the HR-100 instruments. This difference is most likely due to instrumental errors.

In Run III-43, .0130 mole of tetrabutylammonium 4-methylbenzenesulfinate was added. Pentane had to be used in the extraction procedure, instead of methylene chloride, as the quarternary salt cannot be readily extracted from the latter solvent by water. This change in extraction solvent means that the amount of 2-p-methoxyphenyl-2-propyl ethyl ether measured by the n.m.r. instrument may be less than the amount actually produced in the reaction, due to its partial loss during the removal of the pentane. The pentane was removed at the water pump, and the flask was evacuated for one minute only to minimize the loss of 2-p-methoxyphenyl-2-propyl ethyl ether. A known amount of ethylene carbonate (internal standard) was added and the n.m.r. spectrum recorded at 60 and 100 Mc. (deuterio**chloroform**). The results obtained are recorded in Table XXXV. 2-p-Methoxyphenyl-2-propyl 4-methylphenyl sulfone shows a signal due to the aromatic methyl group 18 c.p.s. down-field from the two methyl groups of the 2,6-dimethylphenyl sulfone at 100 Mc. A very small signal was observed in that region, which would correspond to only .2% of the 4-methylphenyl sulfone based on starting arenesulfinate ester, or a maximum of one per cent of the total amount of sulfones formed.

TABLE XXXV

SUMMARY OF PRODUCT RUNS ON 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENE-SULFINATE IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE

Run	Ester 10 ³ , M	Per cent Ether		Per cent Sulfone	
		at 60 Mc.	at 100 Mc.	at 60 Mc.	at 100 Mc.
III-41	1.129	68.9		15.2	
III-42	1.114	72.8	77.2	20.0	21.3
III-43 ^a	1.120	82.8	73.0	15.1	17.8

^a 0.26 molar tetrabutylammonium 4-methylbenzene sulfinate **present**. Pentane used in extraction.

Reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzene-sulfinate (.02261 M) in anhydrous acetic acid at 25° in the presence of sodium acetate (.0560 M) was allowed to proceed for 40 minutes.

The actual rate constant for this reaction has not been measured but a number of estimates of the rate can be made. Under the above conditions, 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate has a rate constant of 4.2×10^{-6} sec.⁻¹. If we allow a factor of 10^3 for the effect of the p-methoxy group, a first-order rate constant of 4.2×10^{-3} sec.⁻¹ would be predicted for 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzene-sulfinate. (In 90% acetone, 2-p-methoxyphenyl-2-propyl chloride solvolyzes 3360 times faster than 2-phenyl-2-propyl chloride (53). Thus 40 minutes would represent at least 12 half-lives for the reaction of the arenesulfinate ester in anhydrous acetic acid. The above estimate must be a maximum estimate for the half-life, since the factor of 10^3

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might be too low. Alternatively, based on the first-order rate constant of $2.1 \times 10^{-3} \text{ sec.}^{-1}$ for 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 25° , one can predict an acetolysis rate constant of ca. $5 \times 10^{-2} \text{ sec.}^{-1}$. The acetolysis of arenesulfinate esters has been found to be 25-35 times faster than their ethanolysis (46). The rate constant of $5 \times 10^{-2} \text{ sec.}^{-1}$, corresponds to a half-life of ca. 14 seconds, thus 40 minutes would be equivalent to 170 half-lives for the reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 25° . Therefore, under either set of assumptions, the reaction must have proceeded to completion.

The same workup procedure was employed as in the ethanolysis, using pentane for the extraction. The n.m.r. spectrum was recorded at 100 Mc. in CDCl_3 solution, and the area ratios obtained correspond to 27.8% 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone. The n.m.r. spectrum also shows minor amounts of 2-p-methoxyphenylpropene and 2,6-dimethylphenyl 2,6-dimethylbenzene thiol-sulfonate, but the sum total of the above compounds does not exceed 40% based on starting arenesulfinate ester. It is possible that a portion of 2-p-methoxyphenylpropene and all of the 2-p-methoxyphenyl-2-propyl acetate was lost during the procedure used for the measurement of the sulfone.

In run III-45, the arenesulfinate ester (.02266 M) was allowed to react in anhydrous acetic acid in the presence of sodium acetate (.0560 M) and tetrabutylammonium 4-methylbenzenesulfinate (.267 M). The n.m.r. spectrum recorded at 100 Mc. in CDCl_3 showed the presence of 26.7% 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, and minor amounts of olefin and thiol-sulfonate. The maximum amount of

2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone formed would be less than 1% as measured by a very weak signal 18 cps. down-field from the aromatic methyl groups or 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone.

In control run III-49, .0345 g. (1.085×10^{-4} mole) of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone and .0062 g. (2.04×10^{-5} mole) of 2-p-methoxyphenyl-2-propyl 4-methylphenylsulfone were dissolved in 50 ml. of anhydrous acetic acid (.0560 M in sodium acetate), and placed in the 25° constant temperature bath for 40 minutes. After the usual workup, the n.m.r. spectrum was recorded at 100 Mc. in CDCl_3 and from the area ratio of component to internal standard the amount of each sulfone recovered was calculated. Analysis indicated 90%, (9.25×10^{-5} mole) of the 2,6-dimethylphenyl sulfone and 104% (2.13×10^{-5} mole) of the 4-methylphenyl sulfone were recovered. This experiment shows that substantially all of the sulfone mixture is recovered and analyzed by the method used.

In Table XXXVI a summary of the product runs on the different arenesulfinate esters is given.

TABLE XXXVI

SUMMARY OF PRODUCT RUNS ON PARA-SUBSTITUTED 2-PHENYL-2-PROPYL 2,6-DI-METHYLBENZENESULFINATES IN ANHYDROUS ETHANOL AT 90.0°.

Compound	Run No.	% Olefin	% Ether	% Sulfone	Total
2-Phenyl-2-propyl 2,6-dimethylbenzene- sulfinate	I-208	38.0	51.0	9.7	98.7
	I-217	38.0	50.8	9.6	98.4
2-p-Bromophenyl-2- propyl 2,6-dimethyl benzenesulfinate	III-5	41.8	48.7	8.4	98.9
2-p-Tolyl-2-propyl 2,6-dimethylbenzene- sulfinate	III-16	30.3	53.9	14.4	98.6
2-p-Methoxyphenyl- 2-propyl 2,6-dimethyl- benzenesulfinate ^(a)	III-41		68.9	15.2 ^(b)	84.1
	III-42		77.2	21.3 ^(c)	98.5

(a) at 25.0°; no olefin was detected.

(b) Products were not isolated, measured by n.m.r. at 60 Mc.

(c) Products were not isolated, measured by n.m.r. at 100 Mc.

DISCUSSION

Nuclear Magnetic Resonance Spectra of Arenesulfinate Esters

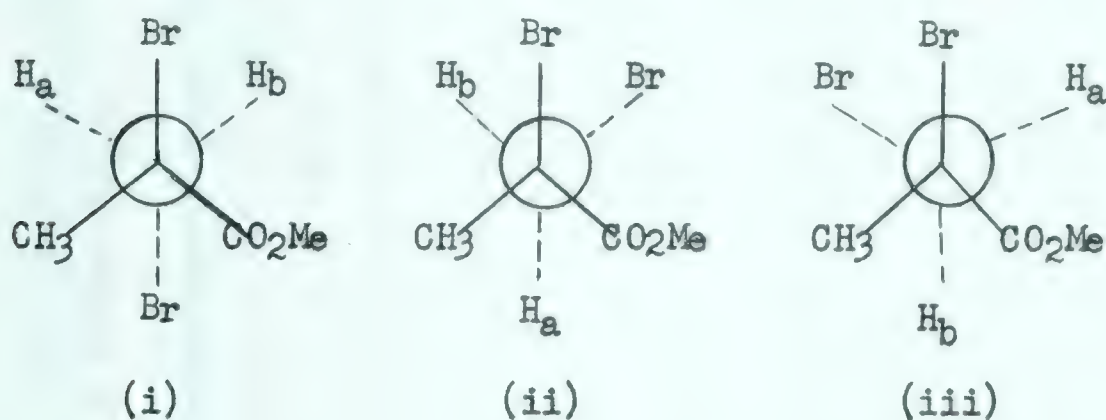
In Chapter I, it was pointed out that in the n.m.r. spectrum of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate, the signal due to the gem-dimethyl group is split into a doublet with a spacing of .17 p.p.m. Similar splitting of the gem-dimethyl signal is observed in the n.m.r. spectra of isopropyl, 2-p-bromophenyl-2-propyl, 2-p-tolyl-2-propyl, 2-p-nitrophenyl-2-propyl and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate as shown in Tables XX and XXXVII. Nair and Roberts (69) have recorded analogous observations in the n.m.r. spectra of gem-difluoro compounds of the type $R_1CF_2CR_2R_3R_4$. They attributed the splitting of the F signal as due to unequal residence time of the molecule in each of the various rotational conformations. Similar conclusions have been reached by Pople (70) and Waugh and Cotton (71).

In the case of ethyl 2,6-dimethylbenzenesulfinate, a single quartet is observed for the methylene protons, while for benzyl 2,6-dimethylbenzenesulfinate only a singlet for the methylene protons is recorded.

In contrast to this, the ethyl esters of benzenesulfinic, p-toluenesulfinic, o-toluenesulfinic and o-chlorobenzenesulfinic acids exhibit a more complex spectrum in the methylene region as shown in Table XXXVII (16). Similarly, a doublet has been observed for the methylene protons of benzyl benzenesulfinate (72). Waugh and Cotton (71) have interpreted the n.m.r. spectrum of ethyl benzenesulfinate in the methylene region to be composed of a pair of non-equivalent protons,

split almost to the same extent by the methyl protons. The n.m.r. spectra of ortho and para substituted ethyl benzenesulfonates may be interpreted exactly the same way as that of ethyl benzenesulfonate.

Jackman (73) has considered the system, $-\text{CH}_2-\text{CRST}$ in which the methylene group is adjacent to an asymmetric carbon atom. Illustrated below are three conformations of methyl 2,3-dibromo-2-methylpropionate. It is apparent that H_a and H_b are not in the same environment in



confirmations (i) and (ii). The non-bonded interactions due to the two bromine atoms are different in the two conformations, thus different distortions and polarizations may result. Even if free rotation is permitted, and the different conformations are equally populated, the shielding of H_a is not necessarily equal to that of H_b .

The above mentioned arenesulfonate esters are similar to Jackman's example, except that the gem-dimethyl group is located one atom further from the asymmetric center, the sulfur atom.

Therefore, it appears that the only anomalous spectra recorded are those in which there is a methylene group next to the oxygen atom of the 2,6-dimethylbenzenesulfonate group. It is possible that the effect of the 2,6-dimethylphenyl group is such as to cause an "accidental" equivalence in the shielding of the methylene protons. An alternate view

TABLE XXXVII

SUMMARY OF THE METHYL AND METHYLENE PROTON SIGNALS FROM THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF CERTAIN ARENESULFINATE ESTERS (CS₂).

Compound	J (a)	
	gem-dimethyl	$\begin{array}{c} \text{---CH}_2\text{---} \\ \text{---CH}_3 \end{array}$
2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate	8.18, 8.35 (s)	
2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate	8.18, 8.35 (s)	
2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate	8.18, 8.35 (s)	
2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate	8.18, 8.35 (s)	
2-p-Nitrophenyl-2-propyl (b) 2,6-dimethylbenzenesulfinate	8.03, 8.14 (s)	
Ethyl 2,6-dimethylbenzene- sulfinate(c)	5.98 (q)	8.70 (t)

continued.

TABLE XXXVII continued.

Compound	$\overbrace{\text{gem-dimethyl}}^{\text{---}}$	$\overbrace{\text{---CH}_2\text{---}}^{\text{---}} \text{---CH}_3$
Isopropyl 2,6-dimethyl- benzenesulfinate (c)	8.62, 8.74 (d)	-CH 5.50 (sept)
Benzyl 2,6-dimethyl- benzenesulfinate	5.11 (s)	
Ethyl 2-methylbenzene- sulfinate (d)	6.32 (m)	8.87 (t)
Ethyl 4-methylbenzene- sulfinate (d)	6.30 (m)	8.83 (t)
Ethyl benzene- sulfinate (d)	6.28 (m)	8.83 (t)
Ethyl 2-chlorobenzene- sulfinate (d)	6.18 (m)	8.78 (t)

(a) Chemical shifts are recorded in p.p.m. on the τ scale.(b) in CDCl_3 .(c) in CCl_4 .

(d) Data from reference 16.

would be that the bond angles of the asymmetric sulfur atom are distorted from their normal values, making the molecule more nearly planar, and in the process the methylene groups may become magnetically equivalent. It is also possible that the 2,6-dimethylphenyl group distorts the shape of the entire molecule, and in the process the magnetic non-equivalence is lost.

The Nature of Intermediates in the Ionization of *para*-Substituted
2-Phenyl-2-propyl 2,6-Dimethylbenzenesulfinates

It has been shown previously that 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate undergoes reaction in a variety of solvents by ionization, and that the 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone is formed by ion pair return. We shall now examine the reactions of *para*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinates.

Sulfur-oxygen bond cleavage has been considered and concluded to be negligible in the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in a number of solvents. Of the arenesulfinate esters studied, sulfur-oxygen bond cleavage is most likely to take place in the reaction of 2-*p*-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol, i.e., the least reactive ester towards carbon-oxygen bond fission.

It has been pointed out in the results section that measurement of the rate of reaction of 2-*p*-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate is beset by a number of difficulties. In the ethanolysis of this ester, the rate constant measured by titrimetry exhibits a low precision, but is within the limits indicated, the same as the rate constants measured by n.m.r. spectrophotometry. The rate of arenesulfinate

ester disappearance was also measured by n.m.r. spectrophotometry, and it was found that ethyl 2,6-dimethylbenzenesulfinate is one of the products formed.

Ethyl 2,6-dimethylbenzenesulfinate may be formed by sulfur-oxygen bond cleavage, or through esterification of 2,6-dimethylbenzenesulfinic acid produced in the reaction by carbon-oxygen bond cleavage. Since the ratio of ethyl 2,6-dimethylbenzenesulfinate formed to 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate expended is approximately constant at all times, it is unlikely that the former compound arises through esterification of the 2,6-dimethylbenzenesulfinic acid. Therefore, ca. 27% of the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° proceeds by sulfur-oxygen bond cleavage.

Since ca. 27% of the reaction proceeds by sulfur-oxygen bond cleavage, the rate constant for ethyl 2,6-dimethylbenzenesulfinate formation is ca. $1.3 \times 10^{-6} \text{ sec.}^{-1} \times .27 = 3.5 \times 10^{-7} \text{ sec.}^{-1}$.

We have earlier used the rate constant for the reaction of benzyl 2,6-dimethylbenzenesulfinate as an estimate of the upper limit for the rate constant for sulfur-oxygen bond cleavage in 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. The presence of a p-nitro group in 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate should accelerate the rate of sulfur-oxygen bond cleavage **by no more than a factor of ten.** As an example of the effect of a p-nitro group, the alkaline hydrolysis of p-nitrobenzyl acetate is 4.4 times faster than that of benzyl acetate in 56% (by weight) aqueous acetone at 0° (74). If as a rough estimate each methyl group retards the rate of sulfur-oxygen bond cleavage by a factor

of three, the retarding effect of the two methyl groups would cancel the accelerating effect of the p-nitro group. Thus, approximately the same rate constant would be predicted for sulfur-oxygen bond cleavage in benzyl 2,6-dimethylbenzenesulfinate and 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate, under identical conditions. The rate constant for the reaction of benzyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° in the presence of 2,6-lutidine is ca. $2 \times 10^{-7} \text{ sec.}^{-1}$ (63). Under identical conditions the rate constant for sulfur-oxygen bond cleavage for 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate is $3.5 \times 10^{-7} \text{ sec.}^{-1}$, which is in good agreement with the predicted value.

The measurement of the rate of acid production in the ethanolysis of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate is rather inaccurate. However, a consideration of the amount of acid produced leaves no doubt that a substantial portion of it must have been formed by carbon-oxygen bond cleavage of the arenesulfinate ester. Since ca. 27% of the arenesulfinate ester reacts by sulfur-oxygen bond cleavage, the maximum value for the solvolysis rate constant is $9.5 \times 10^{-7} \text{ sec.}^{-1}$.

($k_{\text{solv.}} = k_{\text{obs.}} F_{\text{solv.}}$) Therefore, both carbon-oxygen and sulfur-oxygen bond cleavage take place in the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90°.

It is interesting to note that the previous models used, benzyl 2,6-dimethylbenzenesulfinate and p-methoxyneophyl 2,6-dimethylbenzenesulfinate, did in fact provide a reasonable upper and lower limit for the rate of sulfur-oxygen bond cleavage in 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. The rate of sulfur-oxygen bond cleavage for

2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate may now be used to gauge the rate of sulfur-oxygen bond cleavage in other 2-aryl-2-propyl 2,6-dimethylbenzenesulfinate esters. The rate of sulfur-oxygen bond cleavage in the other arenesulfinate esters studied must be slower than that found for 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate. The rate constants for arenesulfinate ester disappearance of 2-p-bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate, 2-p-tolyl-2-propyl 2,6-dimethylbenzenesulfinate and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° in the presence of 2,6-lutidine are 7×10^{-5} , 3.7×10^{-3} and $6.8 \times 10^{-1} \text{ sec.}^{-1}$ (extrapolated from data of 0° and 25°) respectively. These rate constants are ca. 2×10^2 , 10^4 , and 10^6 times faster than the rate constant for sulfur-oxygen bond cleavage in 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate under identical conditions. Therefore, kinetic data suggest sulfur-oxygen bond cleavage to be unimportant for the above arenesulfinate esters under the conditions studied.

Similar conclusions may be arrived at by considering the results of product analyses. A summary of the product runs carried out on the various arenesulfinate esters in anhydrous ethanol appears in Table XXXVI. The products of 2-p-bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate and 2-p-tolyl-2-propyl 2,6-dimethylbenzenesulfinate were the respective ethyl ether, olefin and sulfone. 2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate yielded only 2-p-methoxyphenyl-2-propyl ethyl ether and 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, no 2-p-methoxyphenylpropene. Ethyl 2,6-dimethylbenzenesulfinate is the expected product from sulfur-oxygen bond cleavage in the reaction of each of the above

arenesulfinate esters in anhydrous ethanol. None of this compound was detected in any of the product runs listed in Table XXXVI.

Therefore, both kinetic data and the results of product isolation experiments show that sulfur-oxygen bond cleavage takes place only in the reaction of 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate.

Correlation of Structure and Reactivity

The correlation of structure and reactivity has been a long desired aim of organic chemists. Hammett (75) found that when the logarithms of rates or equilibrium constants of two different reactions of a series of m- and p-substituted benzene derivatives were compared, a linear relationship existed between them. He chose the ionization of benzoic acids in aqueous solution at 25° as the standard reaction and thus obtained the relationship

$$\log \frac{K}{K_0} = \rho \sigma$$

where σ , the substituent constant, is a measure of the electron-donating or electron-withdrawing ability of the substituent, and ρ is the reaction constant which reflects the sensitivity of the equilibrium or rate constant to changes in the σ value of the substituent. ρ was defined unity for the ionizations of benzoic acids, in water at 25°.

Hammett himself pointed out some of the limitations of the above relationship; it does not hold for o-substituted benzene derivatives, nor for aliphatic systems. Large deviations are caused by resonance interactions between strongly electron-donating or withdrawing substituents and the reaction site. He suggested the use of an alternate set of substituent constants for use in reactions of aniline and phenol

derivatives. Later Taft (76) used a set of σ^- values for substituents capable of strong electron withdrawal.

Brown and Okamoto (26) suggested the use of a modified Hammett relationship for strongly electron donating *p*-substituents in reactions where strong resonance interactions between substituent and reaction site may take place. They based their new scale on the solvolysis rates of 2-phenyl-2-propyl chloride and its derivatives in 90% aqueous acetone. From the plot of the *m*-substituted 2-phenyl-2-propyl chlorides against the Hammett σ values, a ρ value of -4.62 was obtained. Using the modified Hammett relationship, $\log k/\log k_0 = \rho\sigma^+$, and the ρ value of -4.62 from the rate data observed for *m*-substituted halides, σ^+ values were calculated for the *para* substituents. Obviously the linear relationship was still maintained between the logarithm of the rate constants and the new σ^+ values.

These authors also suggested that all of the reactions of *m* and *p*-substituted benzene derivatives may be divided into two broad categories, those in which the σ values are to be used, and those where σ^- or σ^+ may give a better fit.

The above suggestions of Brown and coworkers have been criticized by de la Mare (77) and others. Van Bekkum, Verkade and Wepster (78) have shown that a great number of σ values would be required to correlate data where resonance interactions between substituent and reaction site takes place. They calculated ρ constants for several reactions only using σ values for substituents where large resonance contribution seemed unlikely. From the values of ρ thus obtained, in turn σ values were calculated for each substituent which could have a

large resonance interaction.

According to Brown's suggestion, the σ values obtained for any substituent should fall into two discrete groups, e.g., for nitro $\sigma = .778$ and $\sigma^- = 1.27$. The values calculated by the Dutch workers are spread almost continuously from .766 to 1.378.

In Table XXXVIII the relationship among $\log k_{\text{obs.}}$, $\log k_{\text{solv.}}$ and $\log k_{\text{rear.}}$ and the σ and σ^+ values for *p*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfonates in anhydrous ethanol at 90° is summarized. The data are illustrated in graphical form in Figures XVI, XVII and XVIII. The rate constant for 2-*p*-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfonate has been extrapolated from data at 0 and 25°. It has been assumed that the same amount of rearrangement takes place at 25 and 90° in anhydrous ethanol.

It is readily apparent that a better correlation is obtained with σ^+ than with σ values, for each of the above plots. From the slope of the least squares line, for $\log k_{\text{solv.}}$ versus σ^+ , a $\rho^+ = -3.78$ is obtained. The high negative value of ρ^+ indicates considerable rate acceleration by electron donating groups, and is consistent with the formation of carbonium ion species. This has been earlier pointed out. It is significant that the ρ^+ value for the rearrangement is -4.02, thus the rearrangement reaction to form sulfone is even more strongly influenced by electron donating substituents than the solvolysis, and both must be formed by an ionic process.

TABLE XXXVIII

RELATIONSHIP BETWEEN LOG k 's FOR PARA-SUBSTITUTED 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATES IN ANHYDROUS ETHANOL AT 90.0° AND σ^- AND σ^+ VALUES.

Compound	$k_{\text{obs.}} \frac{1}{\text{sec.}}$	$\log k_{\text{obs.}}$	$\log k_{\text{solv.}}$	$\log k_{\text{rear.}}$	σ	σ^+
2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate	2.25×10^{-4}	-3.66	-3.69	-4.69	0	0
2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate	7×10^{-5}	-4.11	-4.20	-5.20	+0.23	+0.14
2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate	3.7×10^{-3}	-2.43	-2.50	-3.30	-0.17	-0.31
2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate	9.5×10^{-7}	-6.03	-6.03		+0.78	+0.78
2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate	$6.8 \times 10^{-1(a)}$	-0.18	-0.26	-1.86	-0.26	-0.76

(a) Extrapolated from data at 0° and 25.0°.

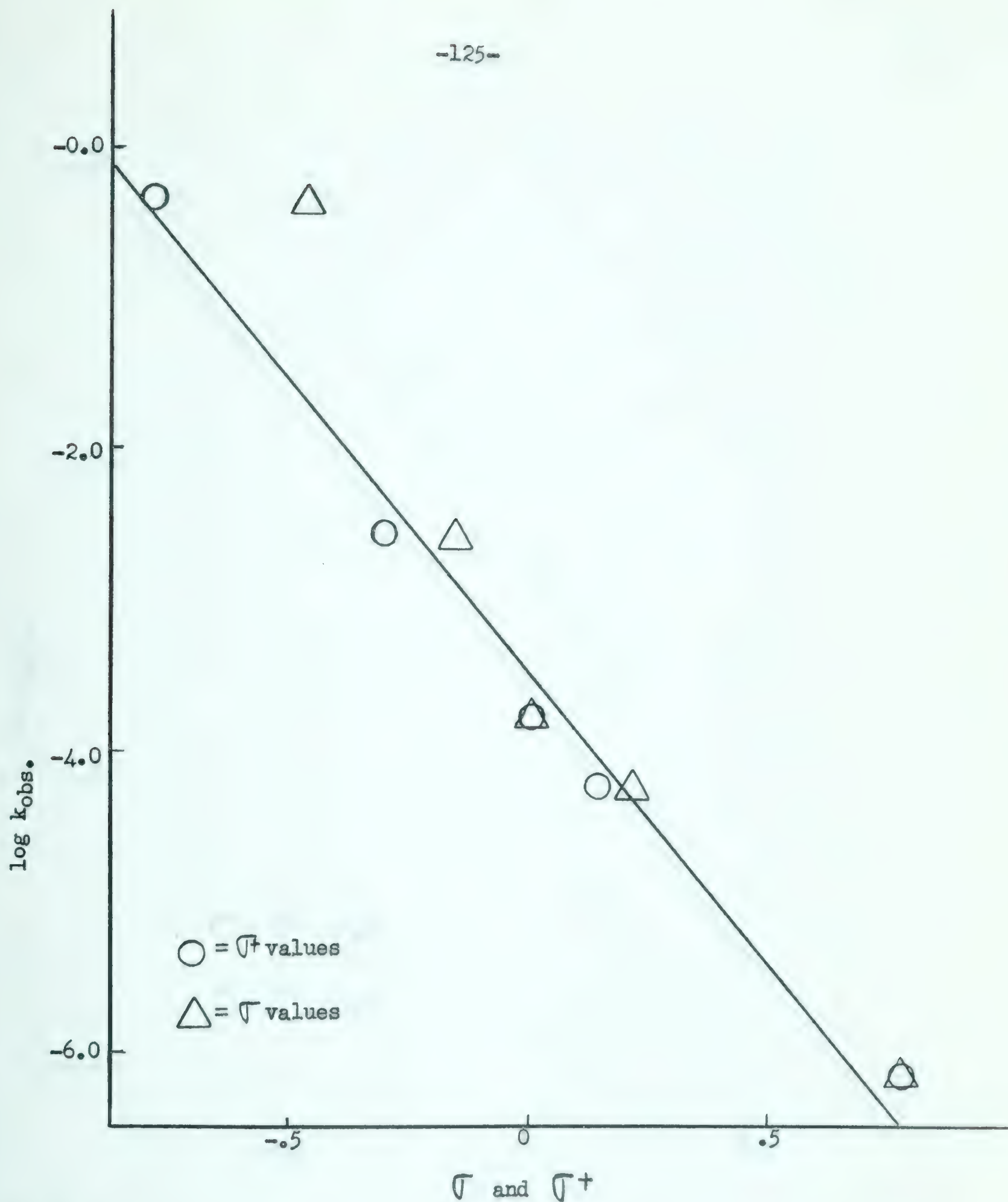


FIGURE XVI

Relationship between $\log k_{obs.}$ and σ and σ^+ values for the solvolysis of *p*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfonates in anhydrous ethanol at 90.0°.

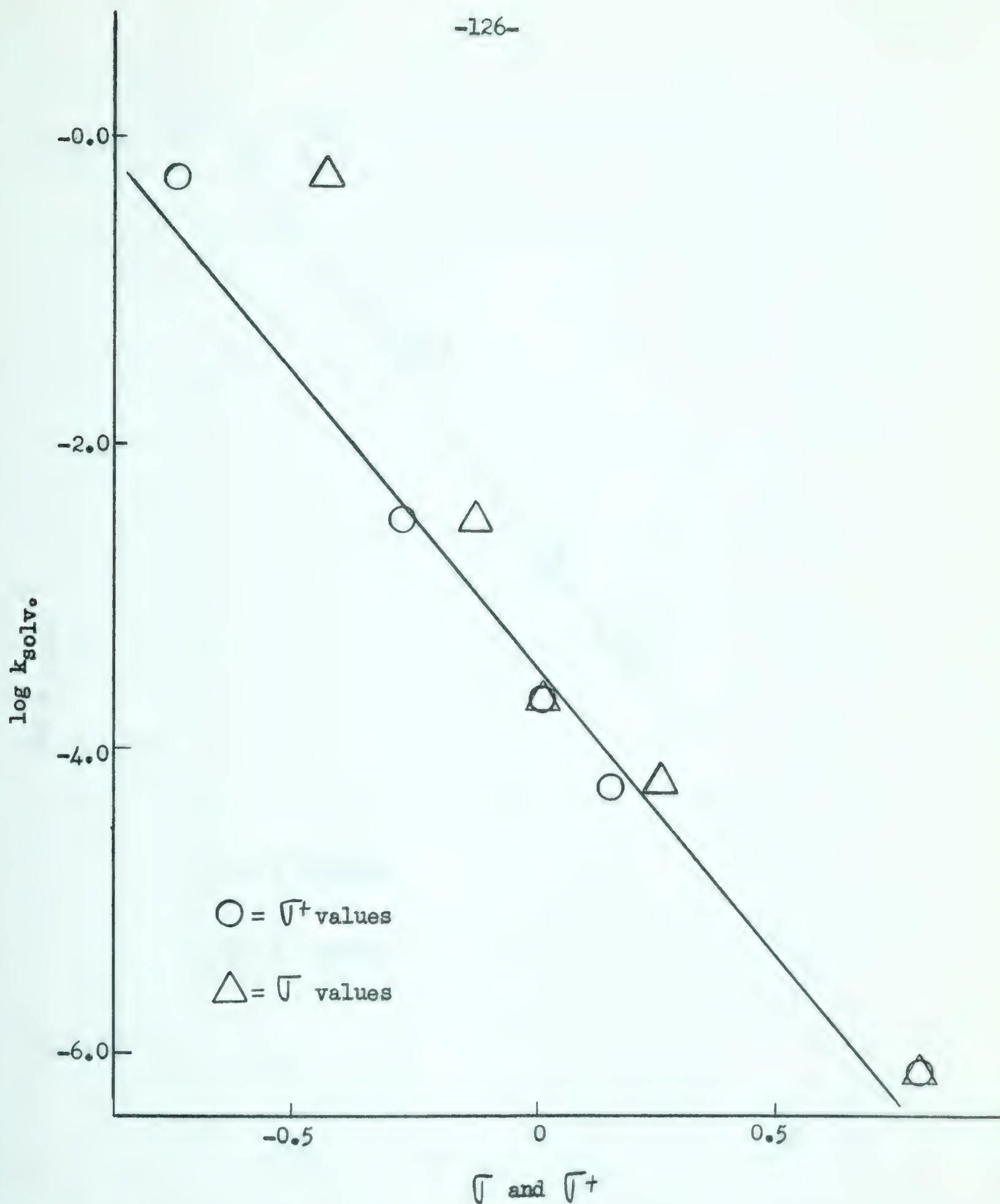


FIGURE XVII

Relationship between $\log k_{\text{solv.}}$ and σ and σ^+ values for the solvolysis of *p*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfonates in anhydrous ethanol at 90.0°.

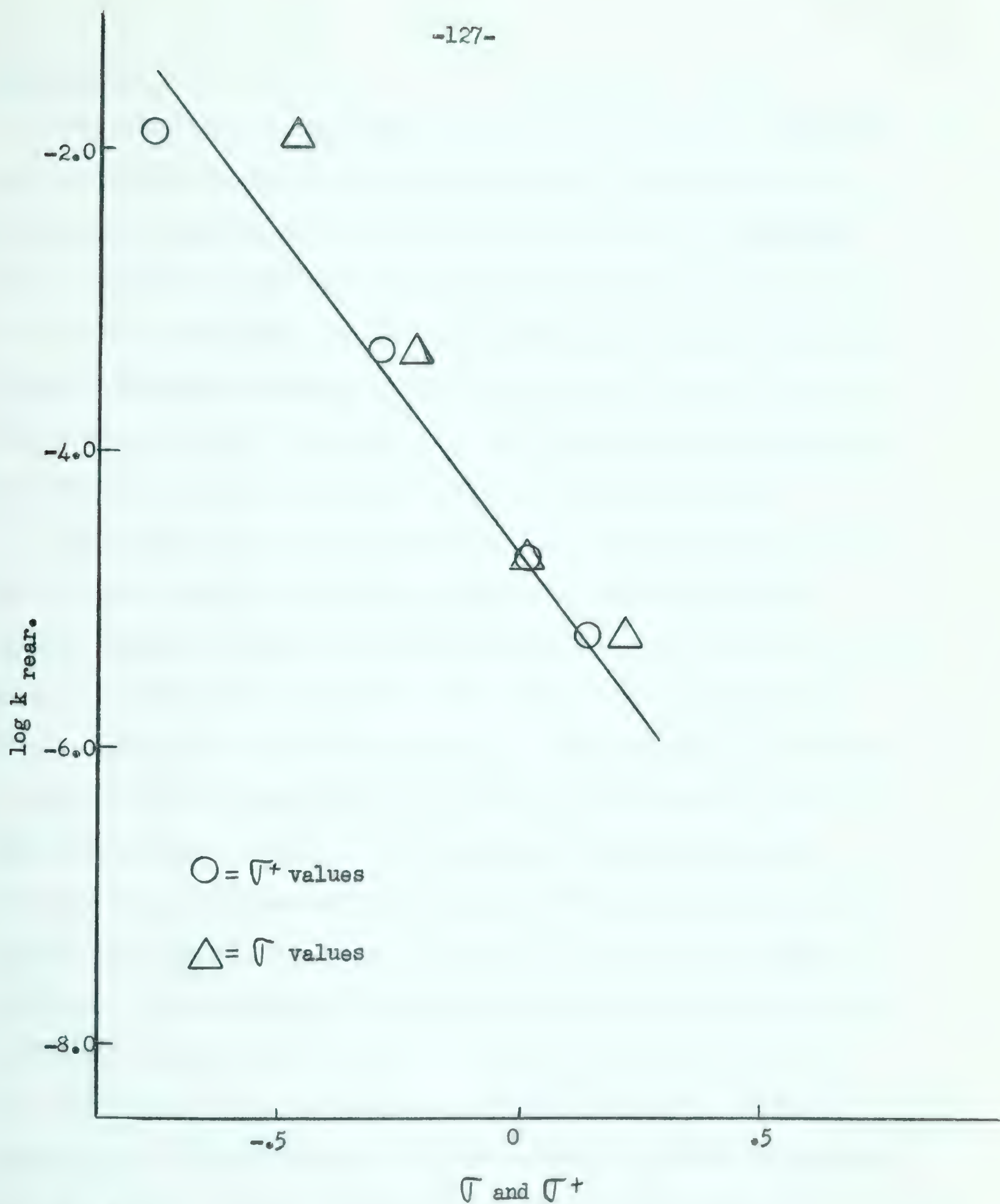


FIGURE XVIII

Relationship between $\log k_{\text{rear.}}$ and σ and σ^+ values for the rearrangement of *p*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinates in anhydrous ethanol at 90.0°.

Salt Effects

An evaluation of salt effects on a reaction is often a powerful tool in the elucidation of reaction mechanisms. In the reaction of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 25°, addition of lithium perchlorate causes a linear acceleration of rate of the order expected for a normal salt effect. The yield of sulfone is somewhat reduced. It is possible that the salt promoted ionization gives rise to a different ratio of solvolysis to rearrangement product, thus a reduced amount of sulfone is isolated (5, 79).

The addition of tetrabutylammonium 2,6-dimethylbenzenesulfinate does not cause common ion rate depression, and the same amount of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone is formed as in the absence of added salt. If sulfone were formed by an intermolecular pathway, addition of 2,6-dimethylbenzenesulfinate ion would be expected to give rise to increased amounts of sulfone, and decreased amounts of solvolysis products. Thus, if the solvent and 2,6-dimethylbenzenesulfinate ion were competing for the same carbonium ion, an increase in sulfone yield would be expected on addition of 2,6-dimethylbenzenesulfinate. Since no change in sulfone yield is discernible, sulfone is not formed from free ions.

Solvolysis of 2-p-methoxyphenyl-2-propyl bromide in anhydrous ethanol at 25° in the presence of tetrabutylammonium 2,6-dimethylbenzenesulfinate yielded at most 1.1% sulfone. Both 2-p-methoxyphenyl-2-propyl bromide and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate yield the same cation on ionization. If the ionization of the two species give the same relative amounts of ion pairs and free ions, and

sulfone is produced exclusively from free ions, the same amount of sulfone should result from each. Since, in the solvolysis of the bromide, a maximum of 1.1% sulfone was obtained, these results indicate that the major portion of the sulfone does not arise from dissociated ions.

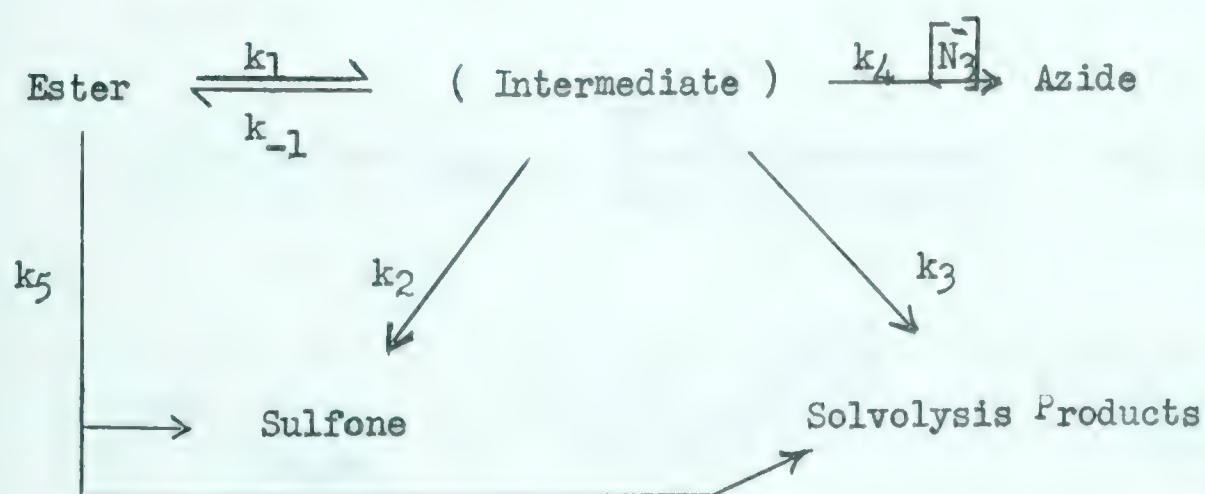
Reaction of the arenesulfinates in the presence of tetrabutylammonium 4-methylbenzenesulfinate, showed no significant change in product formation. If exchange between the ion pair species and the quaternary salt had taken place, 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone should have also been formed. From an examination of the n.m.r. spectrum of the reaction mixture no more than one per cent (absolute) of 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone was formed. Therefore, no significant amount of exchange takes place in sulfone formation.

Since neither common ion rate depression nor exchange is observed, sulfone formation must take place by ion pair return (4). Ion pair return with arenesulfinates results in a rearrangement of the anionic portion of the molecule. This process is similar to randomization of the carboxylate oxygen atoms in p-nitrobenzoates (11) and the thionbenzoate-thiolbenzoate rearrangement (13). The latter two reactions, however, involve a 1,3 shift of the cationic portion of the molecule, while the arenesulfinate ester-sulfone rearrangement consists of a 1,2 shift.

Additional information is obtained from the results of the solvolysis of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol in the presence of tetrabutylammonium azide. As shown in

Table XXVIII addition of the quaternary azide causes a decrease in the amount of solvolysis and rearrangement products formed, and the production of 2-p-methoxyphenyl-2-propyl azide. The effect of azide ion may be within experimental error the same on both solvolysis and rearrangement (Table XXVIII). 2-p-Methoxyphenyl-2-propyl azide may be formed by a direct displacement of sulfinate ion by azide ion, or by reaction of azide ion with carbonium ion or ion pair species. If a displacement reaction were taking place, an increase in the concentration of added azide ion would be expected to give rise to an increase in the rate of reaction. However, the rate constants observed remain constant on changing the azide concentration from zero to ca. .3 M. Therefore, a displacement reaction does not occur, and the 2-p-methoxyphenyl-2-propyl azide must be formed by trapping of ionic species.

We may now set up a reaction scheme as follows:



Here k_5 represents the formation of solvolysis products and sulfone by all other paths than through an intermediate, which is capable of being trapped.

Applying the steady state approximation:

$$\frac{-d [\text{Ester}]}{dt} = k_1 [\text{Ester}] + k_5 [\text{Ester}] - \frac{k_{-1} k_1 [\text{Ester}]}{k_{-1} + k_2 + k_3 + k_4 [\text{N}_3^-]}$$

$$\therefore \frac{d [\text{Azide}]}{dt} = \frac{k_1 k_4 [\text{N}_3^-] [\text{Ester}]}{k_{-1} + k_2 + k_3 + k_4 [\text{N}_3^-]}$$

$$\frac{d [\text{Products}]}{dt} = \frac{k_1 [\text{Ester}] (k_2 + k_3)}{k_{-1} + k_2 + k_3 + k_4 [\text{N}_3^-]} + k_5 [\text{Ester}]$$

$$\frac{[\text{Product}]}{[\text{Azide}]} = \frac{k_2 + k_3}{k_4 [\text{N}_3^-]} + \frac{k_5 (k_{-1} + k_2 + k_3 + k_4 [\text{N}_3^-])}{k_1 k_4 [\text{N}_3^-]}$$

If we define $F_{\text{azide}} = \frac{[\text{Azide}]}{[\text{Azide}] + [\text{Products}]}$ and $k_5 = R k_1$

$$\text{then } \frac{1}{F_{\text{azide}}} = \frac{k_2 + k_3 + k_4 [\text{N}_3^-]}{k_4 [\text{N}_3^-]} + \frac{R k_1 (k_{-1} + k_2 + k_3 + k_4 [\text{N}_3^-])}{k_1 k_4 [\text{N}_3^-]}$$

$$= \frac{(k_2 + k_3 + k_4 [\text{N}_3^-])(1 + R)}{k_4 [\text{N}_3^-]} + \frac{R k_{-1}}{k_4 [\text{N}_3^-]}$$

$$= \frac{R (k_{-1} + k_2 + k_3) + k_2 + k_3}{k_4 [N_3^-]} + (R + 1)$$

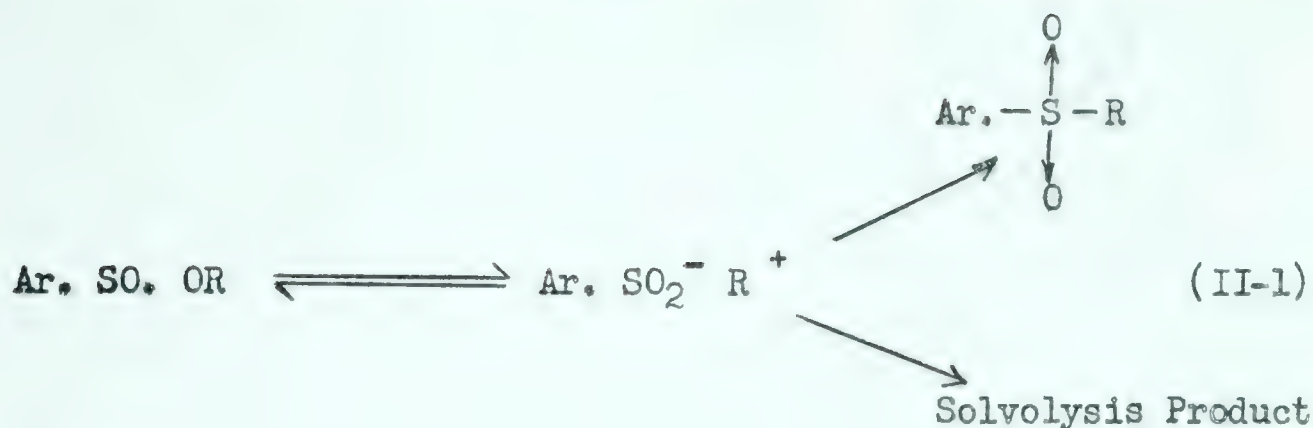
Thus, a plot of $1/F_{\text{azide}}$ against $1/[N_3^-]$ will yield a

straight line with slope $\frac{R (k_{-1} + k_2 + k_3) + k_2 + k_3}{k_4}$

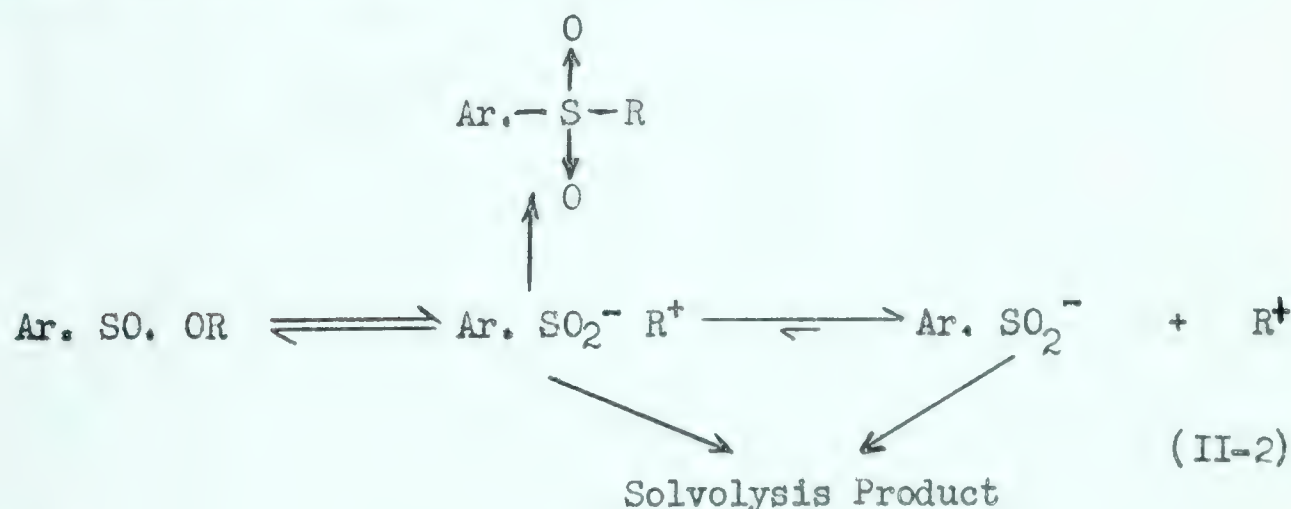
and intercept $(R + 1)$.

Such a plot is given in Figure XIX. The intercept (least squares) is .94 or, within experimental error, one. Thus the value of R must be equal to zero. Therefore, all of the sulfone and the solvolysis product are formed by an ionic pathway, and in principle, they are capable of being trapped completely at sufficiently high azide concentration.

If the effect of azide ion is, in fact, identical on both solvolysis and rearrangement products, then a single common intermediate is the precursor for both solvolysis and rearrangement. It has been shown earlier that sulfone arises by ion pair return, therefore solvolysis product as well must originate from an ion pair. The following mechanism (Equation II-1) for the solvolysis and rearrangement of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol would be consistent with these assumptions.



If, however, the solvolysis product is more effectively trapped than sulfone, a portion of the solvolysis product may arise from dissociated ions, which cannot return to form a significant amount of sulfone. This is shown in Equation II-2, below: In this situation, the relative amounts of solvolysis product arising from ion pairs and dissociated ions are unknown.



We may now consider the effect of added azide ion on the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol. Due to the small amount of rearrangement observed ($9.5 \pm 1.0\%$), the amounts of sulfone measured in the presence of azide ion are subject to relatively large errors. Thus it is difficult to decide whether the decrease in yield of sulfone on addition of azide ion is real, or due to experimental error.

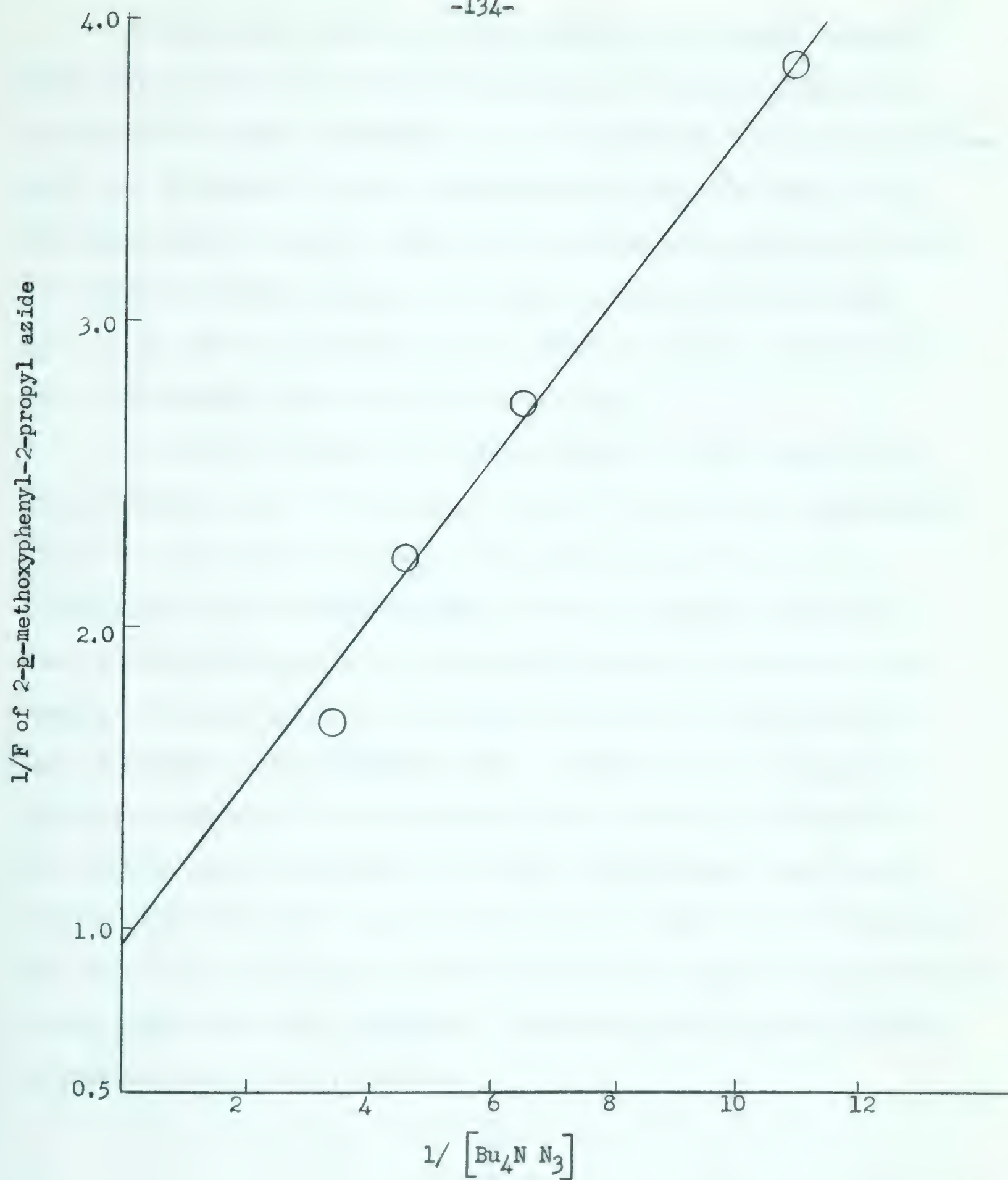
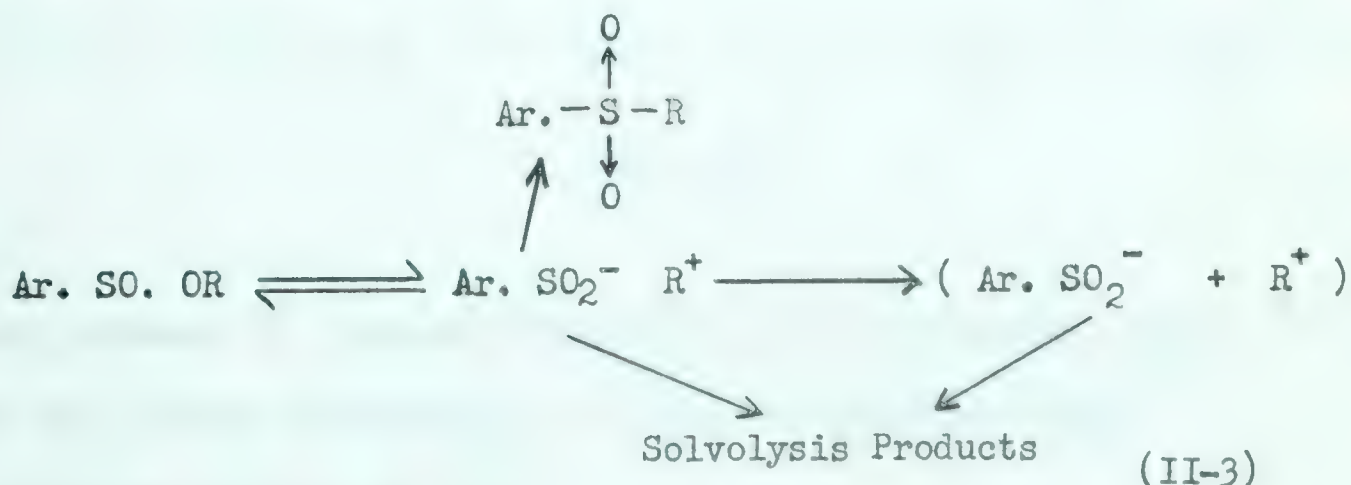


FIGURE XIX

Relationship between the inverse fraction of 2-p-methoxyphenyl-2-propyl azide formed and the inverse concentration of tetrabutylammonium azide added in anhydrous ethanol at 25.0°.

In Figure XX, a plot of inverse fraction of 2-phenyl-2-propyl azide formed against the inverse concentration of tetrabutylammonium azide added is given. An intercept of 2.4 is obtained in the above relationship. Let us consider the same scheme for the reaction of this arene-sulfinate ester, as has been done for 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate on page 130. From the value of the intercept, $k_5 = 1.4 k_1$ and the maximum amount of products trapped by azide ion is 42% at infinitely high azide ion concentration.

If the lower amounts of sulfone isolated in the reaction of the arenesulfinate ester in the presence of azide ion are due to experimental error, then none of the carbonium ion leading to the formation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone is trapped by azide ion. Thus, sulfone would originate exclusively from an ion pair which is not capable of being trapped. The solvolysis products are only trapped in part. A maximum of 42 per cent of the products would be trapped at infinitely high azide ion concentration. The remaining 48 per cent of the reaction which gives rise to solvolysis products must come from a species which cannot be trapped by azide ion. At least one of these species must be an ion pair, while the other may be an ion pair or dissociated ions or both. Thus, with this assumption, the minimum kinetic scheme outlined in Equation II-3, below, results.



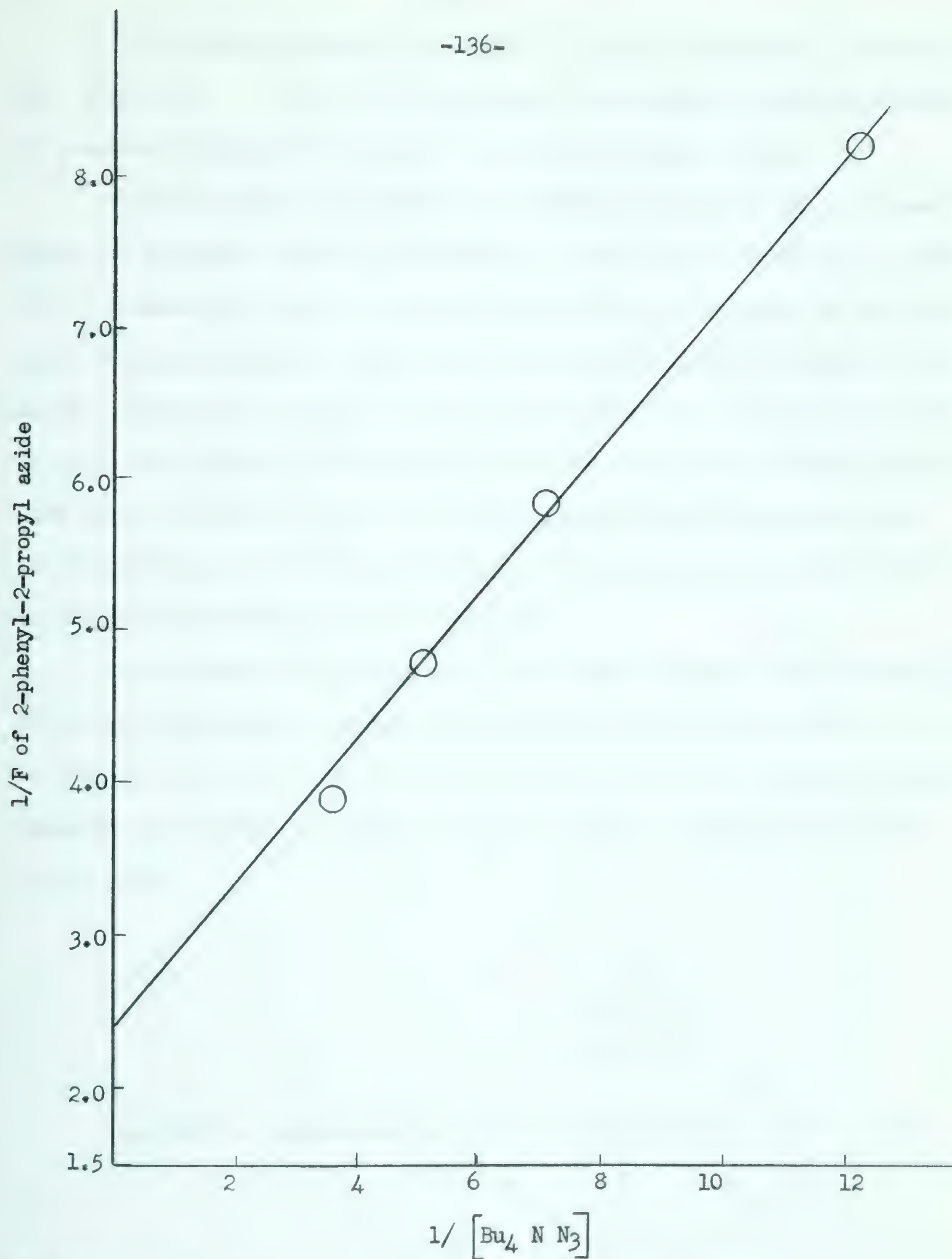


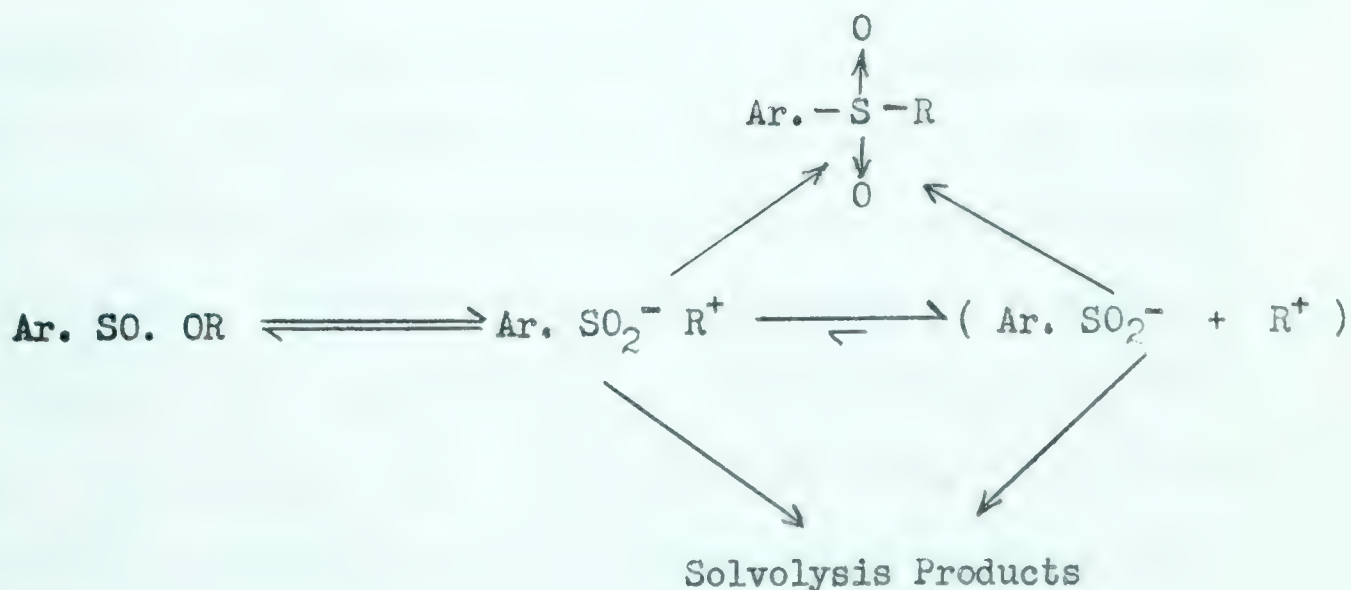
FIGURE XX

Relationship between the inverse fraction of 2-phenyl-2-propyl azide formed and the inverse concentration of tetrabutylammonium azide added in anhydrous ethanol at 90.0°.

In the above scheme, $\text{Ar. SO}_2^- \text{ R}^+$ is a non-capturable ion pair, and $(\text{Ar. SO}_2^- + \text{R}^+)$ is a capturable intermediate, which may either be a solvent separated ion pair, or dissociated ions or both.

If the change in the amount of sulfone isolated in the presence of azide ion is real (9.5% in the absence of azide ion, 7.1% in the presence of .3 M azide ion), then a portion of the sulfone is trapped by azide ion, while the major portion is not. The minimum modification to Equation II-3 is the inclusion of a route for sulfone formation which can be intercepted by azide ion. This is illustrated in Equation II-4. Both of these schemes have been written with the same non-capturable intermediate giving rise to both sulfone and solvolysis products. These species may not be identical, but we have no evidence on this question.

In any case, any scheme which is written requires that a substantial portion of solvolysis products originate from an intermediate which cannot be trapped, and must be an ion pair species. This is an unequivocal demonstration of a reaction in which solvolysis products arise directly from an ion pair.



(II-4)

The results at hand show that substantial amount of ion pair return takes place to the sulfur atom to form 2-phenyl-2-propyl and 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfones. We have no data available on the extent of return to oxygen, to reform starting arenesulfinate ester.

McLaren (24) has studied the solvolysis and rearrangement of α -phenylethyl 2,6-dimethylbenzenesulfinate. Since the above molecule contains two asymmetric centers, (sulfur atom and methine carbon atom), it can exist in two diastereomeric forms. The two diastereomers can be distinguished by means of their n.m.r. spectra. When solvolysis of the pure diastereomer in 80% ethanol was carried to 50 per cent completion, and the arenesulfinate ester isolated, some of the other diastereomer was found to be present. These results indicate substantial return to oxygen.

In the case of the 2-aryl-2-propyl 2,6-dimethylbenzenesulfinate ^{18}O labelling of the arenesulfinate ester may provide a minimum estimate of the return to oxygen, by examining the amount of ^{18}O scrambled in the starting material after a specified time. It is not known whether the two oxygen atoms of the arenesulfinate ester ion pair are equivalent. If the two oxygen atoms were equivalent, return to each oxygen would be equally probable. If this is true, one can gauge the ionization rate, by the sum of the rates solvolysis, sulfone formation and ^{18}O scrambling. On the other hand, if the two oxygen atoms in the sulfinate ion of an ion pair are not equivalent, the amount of ion pair return to give the starting arenesulfinate ester might be quite high. In such a situation the ionization rate would be significantly higher than

the sum of the rates of solvolysis, sulfone formation and ^{18}O exchange.

Comparison of Sulfone Yields Obtained from Various Arenesulfinate Esters

In Table XXXIX a summary of sulfone yields of various arene-sulfinate esters is given. We can first compare systems with constant steric requirement but of different carbonium ion stability. If 2-*p*-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate is excluded, the sulfone yields of the *p*-substituted 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate vary from 9 to 21%. Electron donating groups give rise to higher percentage sulfone values than electron withdrawing groups. Thus, 2-*p*-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate gives more than twice as much sulfone as 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 25°. Therefore, when steric requirements are held constant, the more stable carbonium ion gives rise to higher amounts of sulfone.

In a comparison of the different arenesulfinate esters with approximately the same carbonium ion stability, but of different steric requirements, the amount of sulfone formed decreases in the order benzhydryl > 2-phenyl-2-propyl > α -phenylethyl > *t*-butyl (Table XXXIX). Since the electronic effect of two methyl groups should be roughly equivalent to a phenyl group, one would expect the same amount of sulfone to be formed from benzhydryl and 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate, provided electronic effects only influence sulfone formation. Instead, 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol yields 9.5% sulfone, while benzhydryl 2,6-dimethylbenzenesulfinate under the same conditions gives rise to 35% sulfone. Thus, the steric effect of the methyl groups in

TABLE XXXIX

SUMMARY OF THE AMOUNT OF SULFONE FORMED IN THE REACTIONS OF ARENESULFINATE ESTERS IN THE PRESENCE OF ADDED 2,6-LUTIDINE AT 90.0°.

Compound	Solvent	F _{sulfone}
t-Butyl 2,6-dimethylbenzenesulfinate ^(a)	60% EtOH	0.01
Benzhydryl 2,6-dimethylbenzenesulfinate ^(a)	Anhyd. EtOH ^(b)	.35
	80% EtOH	.37
α-Phenylethyl 2,6-dimethylbenzenesulfinate ^(c)	Anhyd. EtOH ^(b)	.05
	60% EtOH	.12
α-(p-Methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinate ^(c)	Anhyd. EtOH	.27
2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate	Anhyd. EtOH	<.01
2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate	Anhyd. EtOH	.09
2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate	Anhyd. EtOH ^(d)	.09
	80% EtOH	.16
2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate	Anhyd. EtOH	.13
2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate	Anhyd. EtOH ^(e)	.21

(a) Data from reference 46.

(b) In presence of potassium acetate.

(c) Data from reference 24.

(d) At 25.0 and 90.0°.

(e) At 25.0°.

2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate must diminish the amount of sulfone formed. Similar conclusions may be arrived at by comparing the amount of sulfone formed from α -phenylethyl and t-butyl 2,6-dimethylbenzenesulfinate. Both arenesulfinate esters should give rise to carbonium ions of comparable stability, but of different steric requirements. Once again, smaller amount of sulfone results from the carbonium ion of greater steric requirements.

On the basis of carbonium ion stability, one would expect more sulfone to be formed from 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate than from α -phenylethyl 2,6-dimethylbenzenesulfinate. This expectation is borne out by the experimental results. However, substitution **by** the p-methoxy group, causes the sulfone yield to change from 5 to 27% with α -phenylethyl 2,6-dimethylbenzenesulfinate, and from 9 to 20% with 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. Thus, once more steric effects become pronounced, and retard the sulfone formation in the case of 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate. Therefore, both steric and electronic considerations influence the amount of sulfone obtained in the reaction of the corresponding arenesulfinate ester.

EXPERIMENTAL

Physical measurements

Melting points were measured on a Herschberg melting point apparatus, using a set of Anschutz thermometers, which were calibrated against N.B.S. melting point standards. The melting points reported are corrected values.

Refractive indices were obtained on a Bausch & Lomb, Abbe-3L Refractometer, thermostated at 25°.

Infrared spectra were recorded on Perkin Elmer Recording Infrared Spectrophotometers, Models 21, 221G and 421, using sealed sodium chloride cells. The Model 21 was used for all kinetic measurements, except on the 2-p-methoxyphenyl-2-propyl system, where Model 421 was employed. The transmittance due to 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone was measured at 660 cm^{-1} , where the Model 421 has much higher sensitivity.

Nuclear magnetic resonance spectra were recorded on a Varian Analytical Spectrophotometer Model A-60 and HR-100.

For gas chromatography, a Perkin Elmer Model 154D Vapor Fractometer was used.

SOLVENTS

Ethyl alcohol

Anhydrous ethanol was prepared by treatment of 95% ethanol with calcium oxide lumps, followed by reaction with magnesium turnings according to the method of Lund and Bjerrum (64). Karl Fischer titration of various

batches showed no more than .004% water.

Dioxane

Anhydrous dioxane was prepared by the method of Fieser (65), and stored over cleaned sodium. Karl Fischer titration of the purified material showed the presence of less than .005% water.

Acetic Acid

Acetic acid, .1 M in acetic anhydride, was prepared according to the procedure of Fainberg and Winstein (51).

Pentane

Phillips Petroleum technical grade pentane was refluxed for 12 hours with and distilled from phosphorous pentoxide.

Diethyl Ether

Mallinckrodt AR anhydrous ether was used.

Mixed Solvents

Aqueous ethanol and dioxane solutions were prepared by mixing of appropriate volumes of solvent and boiled, distilled water as measured by automatic pipette at 25°. The composition of mixtures recorded is volume per cent, e.g. 80% ethanol means four volumes of anhydrous ethanol mixed with one volume of distilled water.

Standard Base

A sodium methoxide solution was prepared by the addition of the appropriate amount of freshly cleaned sodium to 4 liters of Fisher anhydrous methanol. The resultant solution was standardized against B.D.H. primary

standard potassium hydrogen phthalate, using phenolphthalein as indicator. The solution was kept in a dark, tightly-stoppered bottle and showed no change in titer during four years of use.

2,6-Lutidine

Eastman practical grade 2,6-lutidine was dried over potassium hydroxide, followed by refluxing with and distillation from barium oxide. The center cut, b.p. 139-140°(695 mm.); n_D^{25} 1.4954, was stored in a dark bottle over potassium hydroxide. Reported (66) b.p. 143°(760 mm.), n_D^{25} 1.4953.

Pyridine

Eastman White Label (for Karl Fischer titrations) pyridine was stored over potassium hydroxide in a dark bottle.

2-Phenyl-2-propanol

In a two-liter, three-necked flask equipped with stirrer, condenser and dropping funnel, were placed 34.0 g. (1.41 moles) of magnesium ribbon and 300 ml. of ether. A solution of 200 g. (1.42 moles) of methyl iodide in 350 ml. of ethyl ether was added at such a rate as to maintain gentle refluxing. After the addition of the methyl iodide, the dark reaction mixture was cooled to 0° and a solution of 120 g. (1.0 mole) of acetophenone in 300 ml. of ether was slowly added. At the completion of the addition, the reaction mixture was allowed to warm to room temperature and 225 ml. of saturated ammonium chloride solution was added slowly, vigorous stirring being maintained. The ether solution was decanted, and the solid washed three times with 100 ml. portions of ethyl ether. The combined ether solutions were washed twice with 10% sodium carbonate solution,

followed by eight washings with water. The solution was dried over potassium carbonate, the ether removed at the aspirator and the residual pale-yellow solution distilled at reduced pressure under nitrogen to give 90. g.(68%) of a clear-white liquid, b.p. 68-70° (4.2 mm.); n_D^{25} 1.5188, reported (52) b.p. 94° (13 mm.). Infrared (CS₂) : 3580, 3480, 1025, 945, 758, 690 cm.⁻¹; n.m.r. (CS₂) : 3.0 (m), 6.75 (s), 8.65 τ (s), ratio: 5:1:6; (calculated ratio: 5:1:6). The following abbreviations are used in the description of n.m.r. spectra: "m" for multiplet, "s" for singlet, "d" for doublet, "t" for triplet and "q" for quartet.

2-p-Bromophenyl-2-propanol

This compound was prepared by the reaction of p-bromoacetophenone with methylmagnesium iodide in 80% yield; b.p. 104-107° (1.6 mm.); m.p. 45-46° (reported (53) m.p. 45.6°). Infrared (CS₂) : 3580, 1000, 945, 820, 810, 725 cm.⁻¹; n.m.r. (CS₂) : 3.0 (m), 6.75 (s), 8.65 τ (s), ratio: 4:1:6 (calculated ratio: 4:1:6).

2-p-Tolyl-2-propanol

The reaction of p-methylacetophenone and methylmagnesium iodide yielded the desired alcohol in 71% yield; b.p. 70-72° (2 mm.); n_D^{25} 1.5168; (reported (39) b.p. 101° (10 mm.), n_D^{20} 1.5180). Infrared (CS₂) : 3580, 3480, 1015, 945, 810, 720 cm.⁻¹; n.m.r. (CS₂) : 3.0 (q), 6.82 (s), 7.80 (s), 8.65 τ (s), ratio: 4:1:3:6 (calculated ratio: 4:1:3:6).

2-p-Methoxyphenyl-2-propanol

This compound was prepared by the reaction between p-methoxyphenyl-magnesium bromide and acetone, keeping the temperature of the mixture at

all times below 0°. The desired alcohol was obtained in 45% yield; b.p. 110-112° (4.3 mm.); n_D^{25} 1.5270 (reported (54) b.p. 122° (13 mm.)). Infrared (CS₂) : 3580, 3480, 2830, 1240, 1032, 945, 825 cm.⁻¹; n.m.r. (CCl₄) : 3.1 (m), 6.35 (s), 7.21 (s), 8.65 τ (s) ratio: 4:3:1:6 (calculated ratio: 4:3:1:6).

3-Phenyl-3-pentanol

The reaction of diethyl ketone and phenylmagnesium bromide afforded the desired compound in 85% yield; b.p. 64-66° (1.2 mm.); n_D^{25} 1.5141 (reported (56) b.p. 109° (15 mm.); n_D^{20} 1.5165). Infrared (CS₂) : 3595, 955, 750, 692 cm.⁻¹; n.m.r. (CS₂) : 2.85 (m), 7.95 (s), 8.25 (q), 9.30 τ (t), ratio: 4:1:4:6 (calculated ratio: 4:1:4:6).

2-p-Nitrophenyl-2-propanol

A mixture of 85 g. of concentrated nitric acid and 115 g. of concentrated sulfuric acid was added slowly to a vigorously stirred solution of 100 g. (.84 mole) of 2-phenylpropane in a one-liter Erlenmeyer flask, the temperature being maintained between 45-50°. The reaction mixture was allowed to stand for two hours after the completion of acid addition and then poured onto one liter of ice-water. The organic phase was separated, and washed twice with 100 ml. portions of water, three times with 50 ml. portions of 5% sodium carbonate solution, followed by 50 ml. of water. The pale-yellow liquid was dried over magnesium sulfate, filtered, and fractionally distilled to give a center cut, 76 g., b.p. 100-118° (6.0-7.5 mm.), which was a mixture of 2-(p-nitrophenyl)propane and 2-(o-nitrophenyl)propane.

A mixture of 2-(p-nitrophenyl)propane and 2-(o-nitrophenyl)propane

(92 g.) was dissolved in a solution of 350 ml. of acetic acid and 325 ml. of acetic anhydride. Chromium trioxide (45 g.) was added in small portions over a period of five hours, while the temperature was maintained between 25-35°. The solution was poured onto ice-water, 250 g. of sodium carbonate was added and the solution stirred overnight. The resultant solution was extracted three times with ether and the ether extracts washed successively with water, 10% sodium carbonate solution and water. The ether was removed at the aspirator and the residue steamdistilled. The 34 g. quantity of steam-volatile material consisted mainly of unchanged 2-(p-nitrophenyl)-propane and 2-(o-nitrophenyl)propane. To the steam-nonvolatile material ethyl ether was added, the ether layer was separated and dried over magnesium sulfate. The ether solution was filtered and the solvent removed at the aspirator. The residue (43 g.) was chromatographed over 1.5 kg. of Harshaw (AL-0109P/580-003-45) alumina. Elution with 20% ether-pentane yielded 2.0 g. of unidentified material; with 30% ether-pentane 2.9 g. of 2-p-nitrophenyl-2-propyl acetate; with 40% ether-pentane 8.4 g. of p-nitroacetophenone; with 100% ether 28.2 g. of 2-p-nitrophenyl-2-propanol. n_D^{25} 1.5530 (reported (55) n_D^{19} 1.5552). Infrared (CCl_4) : 3618, 3608, 1525, 1350, 960, 760 cm^{-1} ; n.m.r. (CS_2) : 2.4 (m), 8.55 (s), 8.63 τ (s), ratio: 4:6:1 (calculated ratio: 4:6:1).

2-Phenylpropene

2-Phenyl-2-propanol (18 g., .132 mole) was heated overnight on a steam bath with 6 ml. of 85% phosphoric acid. The reaction mixture was poured onto 100 g. of ice-water and 100 ml. of ether. The ether layer was washed three times with water, twice with 10% sodium carbonate solution,

followed by two further washings with water, and dried over magnesium sulfate. After filtration, the ether was removed on the steam bath and distillation of the pale-yellow oil yielded 9.31 g. (60%) of 2-phenylpropene; b.p. 50-52° (12 mm.); n_D^{25} 1.5354 (reported (57) b.p. 54-55° (14 mm.); n_D^{18} 1.5384). Infrared (neat) : 1720, 1625, 1600, 1500, 1280, 1115, 1040, 895, 780, 770, 700 cm^{-1} ; n.m.r. (neat) : 2.7 (m), 4.76 and 5.00 (m), 8.0 τ (d), ratio: 5:2:3 (calculated ratio: 5:2:3).

2-p-Bromophenylpropene

2-p-Bromophenyl-2-propanol (6.2 g., .029 mole) was heated overnight in a 90° constant temperature bath with 1 ml. of 85% phosphoric acid. The method of isolation of the compound was the same as that used for the preparation of 2-phenylpropene. The required olefin (1.27 g., 21%) was obtained, b.p. 64-66° (2.1 mm.); n_D^{25} 1.5798 (reported (59) b.p. 110° (11 mm.), n_D^{20} 1.5835; and (60) b.p. 58-60° (1.8 mm.), n_D^{27} 1.5778). Infrared (CCl_4) : 1480, 1120, 1070, 890 cm^{-1} ; n.m.r. (CCl_4) : 2.7 (m), 4.70 and 4.95 (m), 7.9 τ (d), ratio: 4:2:3 (calculated ratio: 4:2:3).

2-p-Tolylpropene

2-p-Tolyl-2-propanol (11 g., .073 mole) was heated for three hours on the steam bath in the presence of 3 ml. of 85% phosphoric acid. The method of isolation of the compound was the same as that used for the preparation of 2-phenylpropene. The required olefin (3.04 g., 14%) was obtained, b.p. 57-58° (5 mm.), n_D^{25} 1.5331 (reported (61) b.p. 59° (5 mm.), n_D^{25} 1.5350). Infrared (CCl_4) : 1625, 1510, 1370, 890 cm^{-1} ; n.m.r. (CCl_4) : 2.9 (m), 4.75 and 5.10 (m), 7.75 (s), 7.95 τ (d), ratio: 4:2:3:3 (calculated ratio: 4:2:3:3).

2-p-Methoxyphenylpropene

2-p-Methoxyphenyl-2-propanol (3.3 g., .02 mole) was heated for three minutes on the steam bath with 1 ml. of concentrated sulfuric acid. The method of isolation of the compound was the same as that used for the preparation of 2-phenylpropene. The required olefin (.92 g., 31%) was obtained, b.p. 72-74° (5 mm.); m.p. 31-33° (reported (62) b.p. 63.0-63.5° (.5 mm.); m.p. 34°). Infrared (CS₂) : 2820, 1240, 1170, 1030, 875, 825 cm.⁻¹; n.m.r. (CCl₄) : 3.0 (m), 4.8 and 5.1 (m), 6.35 (s), 7.95 (d), ratio:4:2:3:3 (calculated ratio: 4:2:3:3).

2-Phenyl-2-propyl ethyl ether

2-Phenyl-2-propanol (9.8 g., .072 mole) and 90 ml. of anhydrous ethanol were stirred overnight at room temperature in the presence of 2.5 ml. of concentrated sulfuric acid. The reaction mixture was poured onto ice-water and extracted with ether. The ether solution was washed with water, 10% sodium carbonate solution and dried over magnesium sulfate. After filtration, the ether was removed on the steam bath and the residual liquid distilled to yield 5.04 g. (42%) of colorless liquid, b.p. 70-72° (8 mm.); n_D²⁵ 1.4915 (reported (58) b.p. 48.0-49.5° (2.5 mm.); n_D²² 1.491). Infrared (CCl₄) : 1445, 1270, 1170, 1120, 1075, 1040, 965, 695 cm.⁻¹; n.m.r. (CCl₄): 2.7 (m), 6.85 (q), 8.55 (s), 8.90 (t), ratio: 5:2:6:3 (calculated ratio: 5:2:6:3).

2-p-Bromophenyl-2-propyl ethyl ether

A solution of 10 g. (.0465 mole) of 2-p-bromophenyl-2-propanol in 75 ml. of anhydrous ethanol and 3 ml. of concentrated sulfuric acid were allowed to react for 24 hours at 50°. The method of isolation of the compound was the same as that used for the preparation of 2-phenyl-2-propyl ethyl

ether. The clear oil (11.8 g.) was fractionally distilled to yield a center cut (4.07 g., 36%) b.p. 100-102° (3.5 mm.); n_D^{25} 1.5278. Infrared (CCl_4) : 1475, 1385, 1245, 1155, 1060, 1000 $cm.^{-1}$; n.m.r. (CCl_4) : 2.65 (m), 6.85 (q), 8.55 (s), 8.90 \overline{J} (t), ratio: 4:2:6:3 (calculated ratio: 4:2:6:3).

Analysis: Calculated for $C_{11}H_{15}OBr$: C, 54.33; H, 6.22; Br, 32.87

Found: C, 54.34; H, 6.15; Br, 33.26
54.11 5.92

2-p-Tolyl-2-propyl ethyl ether

A solution of 10 g. (.066 mole) of 2-p-tolyl-2-propanol in 110 ml. of anhydrous ethanol and 2 ml. of concentrated sulfuric acid was allowed to react for 16 hours at room temperature. The method of isolation of the compound was the same as that used for the preparation of 2-phenyl-2-propyl ethyl ether. A pleasant-smelling, clear oil (9.2 g.) was obtained which on fractional distillation gave a center cut, 4.73 g. (40%), b.p. 71-72° (3.5 mm.); n_D^{25} 1.4895. Infrared (CCl_4) : 1500, 1380, 1370, 1352, 1250, 1155, 1060, 955 $cm.^{-1}$; n.m.r. (CCl_4) : 2.85 (m), 6.85 (q), 7.70 (s), 8.55 (s), 8.90 \overline{J} (t), ratio: 4:2:3:6:3 (calculated ratio: 4:2:3:6:3).

Analysis: Calculated for $C_{12}H_{18}O$: C, 80.85; H, 10.18

Found: C, 81.05; H, 10.17
81.29 10.22

2-p-Methoxyphenyl-2-propyl ethyl ether

A solution of 4.9 g. (.03 mole) of 2-p-methoxyphenyl-2-propanol in 40 ml. of anhydrous ethanol and .5 ml. of concentrated sulfuric acid was allowed to react for forty minutes at room temperature. The method of isolation of the compound was the same as that used for the preparation of

2-phenyl-2-propyl ethyl ether. A 4.2 g. (72%) quantity of the desired ether was obtained. n_D^{25} 1.5017; infrared (CS_2) : 1500, 1460, 1435, 1382, 1372, 1350, 1300, 1240, 1170, 1060, 1030, 955 cm^{-1} ; n.m.r. (CCl_4) : 3.0 (m), 6.32 (s), 6.88 (q), 8.58 (s), 8.92 τ (t), ratio: 4:3:2:6:3 (calculated ratio: 4:3:2:6:3).

Analysis: Calculated for $C_{12}H_{18}O_2$: C, 74.19; H, 9.33

Found : C, 73.92; H, 9.12
74.13 9.15

2,6-Dimethylthiophenol

This compound was prepared by the method of Tarbell and Fukushima (41) in 35% yield. B.p. 65-67° (3 mm.); n_D^{25} 1.5714. Infrared (neat): 2580, 1455, 1430, 1390, 1055, 1065, 765 cm^{-1} ; n.m.r. (CCl_4) : 3.08 (s), 7.00 (s), 7.70 τ (s), ratio: 3:1:6 (calculated ratio: 3:1:6). The infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly donated by R.A. McLaren.

2,6-Dimethylbenzenesulfinic acid

This compound was prepared by the method of Hanke (27). A 100 g. quantity (.82 mole) of 2,6-dimethylaniline was dissolved in a cold solution of 600 ml. of water and 80 ml. of concentrated sulfuric acid in a two-liter Erlenmeyer flask, equipped with a stirrer. The solution was cooled to below 5° and a solution of 60 g. (.87 mole) of sodium nitrite in 120 ml. of water was added dropwise with stirring. Sulfur dioxide was bubbled through the solution for two hours, while the temperature was maintained below 5°. Copper powder (300 g.) was gradually added, while cooling and SO_2 addition were continued for a further 30 minutes. A cold solution of 100 ml. of concentrated sulfuric acid and 200 ml. of water was added and

the reaction mixture allowed to warm to room temperature. The mixture was filtered (caution: SO_2 !), the copper mat washed with 20-30 ml. of water and the filtrate discarded. The copper mat was washed with 250 ml. of saturated sodium carbonate solution and the resultant oily-green filtrate treated with decolorizing charcoal. The clear-green solution was acidified with cold 50% sulfuric acid until no further precipitation of 2,6-dimethylbenzenesulfinic acid occurred. The tan-colored solid was filtered, washed with a little ice-cold water and dried overnight in a vacuum dessicator over drierite. Yield: 135 g. (80%); m.p. 90-92°. This material was found to be sufficiently pure for preparative use. For use in kinetic runs, it was twice recrystallized from wet ethanol, m.p. 98-99°. Neutralization equivalent: 170.0 (calculated: 170.2); infrared (nujol) : 2480 (broad), 1450, 1050, 995, 820, 765 cm^{-1} ; n.m.r. (pyridine) : -5.65 (s), 7.18 (s), ratio: 1:6 (calculated ratio: 1:6); n.m.r. (CH_3OH) : 2.85 (m), 7.35 (s), ratio: 1:2 (calculated ratio: 1:2).

2-Phenyl-2-propyl 2,6-dimethylphenyl sulfone

2-Phenyl-2-propanol (2.5 g., .0184 mole) and 4 g. of 2,6-dimethylbenzenesulfinic acid (.0235 mole) and 2 g. of sodium formate in 100 ml. of 88% formic acid were stirred for 70 hours at room temperature in a 125 ml. Erlenmeyer flask. The mixture was poured into water and extracted three times with ether. The ether extracts were washed twice with water, five times with 10% sodium carbonate solution, followed by water and dried over magnesium sulfate. Removal of the ether at the water aspirator left 6.5 g. of a pale-yellow solid. Recrystallization three times from ether-pentane afforded 2.78 g. (53%) of white needles. M.p. 152.5-153.0°; infrared (CCl_4): 1450, 1372, 1365, 1308, 1160, 1135, 1120, 1100, 1030, 690, 655, 612 cm^{-1} ;

n.m.r. (CS_2) : 2.8 (m), 7.92 (s), 8.30 τ (s), ratio: 4:3:3 (calculated ratio: 4:3:3).

Analysis: Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{S}$: C, 70.80; H, 6.99; S, 11.12

Found : C, 70.78; H, 6.83; S, 10.89
70.61 6.87 10.61

2-p-Tolyl-2-propyl 2,6-dimethylphenyl sulfone

This compound was prepared in 30% yield by the procedure described for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, except that the reaction was allowed to proceed for 75 minutes. White needles were obtained; m.p. 139.5-140.0°; infrared (CS_2) : 1370, 1360, 1308, 1158, 1115, 1095, 1030, 820, 770, 648, 598 cm^{-1} ; n.m.r. (CS_2) : 3.1 (m), 7.71 (s), 7.92 (s), 8.30 τ (s), ratio: 7:3:6:6 (calculated ratio: 7:3:6:6).

Analysis: Calculated for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{S}$: C, 71.48; H, 7.33; S, 10.60

Found : C, 71.39; H, 7.39; S, 10.55
71.24 7.20 10.67

2-p-Bromophenyl 2,6-dimethylphenyl sulfone

This compound was prepared in 26% yield by the procedure described for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, except that the reaction was allowed to proceed for 49 hours. White needles were obtained; m.p. 148.7-149.0°; infrared (CS_2) : 1380, 1310, 1162, 1120, 1100, 1012, 836, 778, 668, 632 cm^{-1} ; n.m.r. (CS_2): 2.8 (m), 7.85 (s), 8.30 τ (s), ratio: 7:6:6 (calculated ratio: 7:6:6).

Analysis: Calculated for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{SBr}$: C, 55.59; H, 5.21; S, 8.73; Br, 21.76;

Found: C, 55.65; H, 5.15; S, 8.76; Br, 21.96;
55.42 4.99

2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone

This compound was prepared in 47% yield by the method described for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, except that the reaction was allowed to proceed for 25 minutes. White needles were obtained; m.p. 107.5-108.0°; infrared (CS₂) : 1305, 1255, 1188, 1160, 1120, 1040, 834, 768, 660 cm.⁻¹; n.m.r. (CS₂) : 3.1 (m), 6.30 (s), 7.90 (s), 8.35 τ (s), ratio: 7:3:6:6 (calculated ratio: 7:3:6:6).

Analysis: Calculated for C₁₈H₂₂O₃S : C, 67.89; H, 6.96; S, 10.07

Found : C,	67.92;	H,	6.84;	S,	10.84
	67.82		6.96		10.21
					10.33

2-p-Methoxyphenyl-2-propyl 4-methylphenyl sulfone

This compound was prepared in 75% yield by the procedure described for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, except that the reaction was allowed to proceed for 30 minutes. White needles were obtained; m.p. 120-121°; infrared (CS₂) : 1310, 1302, 1260, 1190, 1160, 1130, 1080, 1040, 835, 818, 720, 680, 660, 618 cm.⁻¹; n.m.r. (CS₂) : 2.9 (m), 6.28 (s), 7.65 (s), 8.38 τ (s), ratio: 8:3:3:6 (calculated ratio: 8:3:3:6).

2-Phenyl-2-propyl 4-methylphenyl sulfone

This compound was prepared in 65% yield by the procedure described for the preparation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, except that the reaction was allowed to proceed for 4 hours. White needles were obtained; m.p. 146.5-147.2° (reported (23) m.p. 144-145°). Infrared (CCl₄) : 1310, 1298, 1285, 1155, 1128, 1025, 690, 675 cm.⁻¹; n.m.r. (CS₂) : 2.90 (d), 7.66 (s), 8.35 τ (s), ratio: 3:1:2 (calculated ratio: 3:1:2).

2,6-Dimethylbenzenesulfinyl chloride

Thionyl chloride (10 g., .084 mole) and 30 ml. of pentane were placed in a 125 ml. Erlenmeyer flask, and 9 g. (.053 mole) of 2,6-dimethylbenzenesulfinic acid was added over a period of ten minutes. When the evolution of gas ceased, the solution was filtered through glass wool into a tared 100 ml. round bottom flask. Most of the excess pentane and thionyl chloride were removed at the aspirator, and the solution was pumped overnight at the vacuum pump. The 7.1 g. (.042 mole) of red oil (80%) obtained, was used immediately for the preparation of the esters, as it is very susceptible to hydrolysis. N.m.r. (pyridine) : 7.40τ (s).

2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate

2-Phenyl-2-propanol (4.35 g., .0325 mole) was dissolved in 30 ml. of anhydrous pyridine and cooled in a Dry Ice-acetone bath. A 7.1 g. (.042 mole) quantity of 2,6-dimethylbenzenesulfinyl chloride, dissolved in 30 ml. of pyridine, was added to the alcohol-pyridine mixture. An immediate precipitate of pyridine hydrochloride was formed. The reaction mixture was placed in the refrigerator, (ca. 5°), for two hours and then poured into a mixture of 300 ml. of water-60 ml. of hydrochloric acid. The resultant oily solution was twice extracted with ether. The combined ether extracts were washed with water, 10% sodium carbonate solution until the washings were colorless, and finally again with water. The ether solution was dried over potassium carbonate, filtered, and the solvent removed at the aspirator. Two recrystallizations from ether-pentane gave 6.2 g. (67%) of the desired product; m.p. 82.5-83.0°; infrared (CS₂): 1385, 1370, 1270, 1130, 1045, 940, 840, 775, 750, 705 cm.⁻¹; n.m.r. (CS₂):

2.9 (m), 7.58 (s), 8.18 (s), 8.35 $\overline{\text{T}}$ (s), ratio: 8:6:3:3 (calculated ratio: 8:6:3:3).

Analysis: Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{S}$: C, 70.80; H, 6.99; S, 11.12

Found : C, 70.94; H, 7.36; S, 11.22
71.04 7.30 11.06
11.20

2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate

This compound was obtained in 38% yield by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate.

M.p. 51.5-52.5°; infrared (CS_2) : 1388, 1370, 1275, 1130, 940, 848, 825, 780, 745 cm^{-1} ; n.m.r. (CS_2) : 2.9 (m), 7.55 (s), 7.71 (s), 8.17 (s), 8.35 $\overline{\text{T}}$ (s), ratio: 7:6:3:3:3 (calculated ratio: 7:6:3:3:3).

Analysis: Calculated for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{S}$: C, 71.48; H, 7.33; S, 10.60;

Found : C, 71.30; H, 7.09; S, 10.51;
71.14 7.18 10.68
10.74

2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate

This ester was prepared in 58% yield by the same procedure as used in the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate.

M.p. 85.5-86.5°; infrared (CS_2) : 1390, 1380, 1362, 1262, 1125, 1008, 930, 825, 770, 750, 725, 705 cm^{-1} ; n.m.r. (CS_2) : 2.9 (m), 7.58 (s), 8.18 (s), 8.35 $\overline{\text{T}}$ (s), ratio: 7:6:3:3 (calculated ratio: 7:6:3:3).

Analysis: Calculated for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{SBr}$: C, 55.59; H, 5.21; S, 8.73; Br, 21.76;

Found: C, 55.82; H, 5.38; S, 8.94; Br, 21.84;
55.68 5.31 8.80 21.91

2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate

The desired ester was prepared in 34% yield by the same procedure as used in the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. M.p. 57-58°; infrared (CS₂) : 1385, 1308, 1250, 1180, 1125, 1040, 830, 800, 775, 745 cm.⁻¹; n.m.r. (CS₂ and pyridine) : 6.32 (s), 7.58 (s), 8.18 (s), 8.35 τ (s), ratio: 1:2:1:1 (calculated ratio: 1:2:1:1).

Analysis: Calculated for C₁₈H₂₂O₃S : S, 10.07;

Found : S, 10.26;
10.10;

2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate

This ester was obtained in 44% yield by the procedure as used in the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. M.p. 103.5-104.0°; infrared (CS₂) : 1380, 1360, 1340, 1260, 1125, 1085, 930, 850, 835, 765, 740, 720, 700 cm.⁻¹; n.m.r. (CDCl₃) : 2.9 (m), 7.42 (s), 8.03 (s), 8.14 τ (s), ratio: 7:6:3:3 (calculated ratio: 7:6:3:3).

Analysis: Calculated for C₁₇H₂₂O₄SN: C, 61.24; H, 5.74; N, 4.20;

Found: C, 60.96; H, 5.80; N, 4.07;
61.22; 5.70; 4.10;

Ethyl 2,6-dimethylbenzenesulfinate

This compound was prepared in 65% yield by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. It could also be obtained by attempted recrystallization of 2,6-dimethylbenzenesulfinic acid from 98% ethanol. M.p. 48.5-49.5° (reported (16) m.p. 47.3-48.6°); infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly supplied by J.M. Noreyko.

Isopropyl 2,6-dimethylbenzenesulfinate

This compound was prepared in 65% yield by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. The infrared and n.m.r. spectra were superimposable upon those of an authentic sample, kindly supplied by J.M. Noreyko.

3-Phenyl-3-pentyl 2,6-dimethylbenzenesulfinate

This ester was prepared in 43% yield by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. M.p. 68.0-69.5°; infrared (CS₂) : 1390, 1135, 890, 770, 735, 695 cm.⁻¹; n.m.r. (CS₂) : 2.8 (m), 7.48 (s), 7.85 (m), 9.30 τ (m), ratio: 4:3:2:3 (calculated ratio: 4:3:2:3).

Benzyl 2,6-dimethylbenzenesulfinate

This ester was prepared in 48% yield by the same procedure as used for the preparation of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate. M.p. 43.0-44.0°; infrared (CS₂) : 1375, 1135, 950, 900, 830, 770, 750, 720, 710, 690 cm.⁻¹; n.m.r. (CS₂) : 2.85 (m), 5.11 (s), 7.52 τ (s), ratio: 4:1:3 (calculated ratio: 4:1:3).

2-Phenyl-2-propyl bromide

A 10 g. (.084 mole) quantity of 2-phenylpropene was dissolved in 20 ml. of methylene chloride. The solution was cooled to -20° and anhydrous hydrogen bromide was passed through the solution for 30 minutes. Most of the excess hydrogen bromide and methylene chloride was removed at the aspirator. The residue was pumped at the vacuum pump for about 20 minutes, when no further evolution of gas could be observed. n_D^{25} 1.5673 (reported

(58) n_D^{20} 1.580). Molecular weight by Volhard titration was 203.0 (calculated 199.1, accordingly 98% purity). Infrared (CCl_4) : 1490, 1445, 1382, 1365, 1252, 1118, 1090, 690, 585 cm^{-1} ; n.m.r. (CCl_4): 2.65 (m), 7.92 T(s), ratio: 5:6 (calculated ratio: 5:6).

2-p-Methoxyphenyl-2-propyl bromide

A 5 g. (.03 mole) quantity of 2-p-methoxyphenyl-2-propanol (containing ca. 15% of an impurity, possibly methoxybenzene) was dissolved in 20ml. of methylene chloride, the solution cooled to -20° , and anhydrous hydrogen bromide bubbled through the solution for 30 minutes. The lower aqueous layer was removed with a fine capillary and the solution dried over magnesium sulfate for 20 minutes. The methylene chloride solution was again saturated with hydrogen bromide for 10 minutes, followed by the removal of the solvent and excess hydrogen bromide at the vacuum pump. Molecular weight by Volhard titration was 266.0 (calculated 229.1, accordingly 85.9% purity); n.m.r. (CCl_4) : 2.95 (m), 6.38 (s), 7.92 T(s), ratio: 4.2:3.6:6.0 (calculated ratio: 4:3:6).

2-Phenyl-2-propyl azide

A 10 g. (.154 mole) quantity of sodium azide was dissolved in 40 ml. of water. Acetone, 120 ml., was added forming two liquid phases. A 12.4 g. (.062 mole) quantity of 2-phenyl-2-propyl bromide was added and the vigorously stirred mixture allowed to stand at room temperature for two hours. The reaction mixture was poured into water and extracted three times with ether. The ether extracts were washed with water, 10% sodium carbonate solution and dried over potassium carbonate. After filtration, the ether was removed at the aspirator and 8.8 g. of pale-yellow oil resulted, which showed some

absorption at 3580 cm^{-1} (due to 2-phenyl-2-propanol). Chromatography on alumina, followed by distillation gave 2.65 g. (27%) of the required azide; b.p. $84-85^{\circ}$ (8 mm.); n_D^{25} 1.5195; infrared (CCl_4) : 2100, 1490, 1382, 1362, 1250, 1145, 1025, 690 cm^{-1} ; n.m.r. (CCl_4): 2.75 (m), 8.45 τ (s), ratio: 5:6 (calculated ratio: 5:6).

Analysis: Calculated for $\text{C}_9\text{H}_{11}\text{N}_3$: C, 67.05; H, 6.88; N, 26.07;

Found : C, 67.38; H, 6.75; N, 25.82;
67.52 6.80

2-p-Methoxyphenyl-2-propyl azide

A 4.3 g. (.026 mole) quantity of 2-p-methoxyphenyl-2-propanol was treated with anhydrous hydrogen bromide as described above. The bromide obtained was dissolved in 30 ml. of acetone and the solution added to 25 ml. of a saturated solution of sodium azide in 70% acetone. After 40 minutes, the reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water, 10% sodium carbonate solution and dried over magnesium sulfate. After filtration, the ether was removed at the aspirator to yield 5 g. of yellow oil which was distilled at reduced pressure to give 2.35 g. of 2-p-methoxyphenylpropene, b.p. $72-74^{\circ}$ (5 mm.), and 1.6 g. of a red oil. Chromatography of the red oil over alumina gave .850 g. (17%) of the required azide; n_D^{25} 1.5312; infrared (CCl_4) : 2100, 1600, 1500, 1455, 1360, 1295, 1240, 1172, 1138, 1030 cm^{-1} ; n.m.r. (CCl_4) : 3.0 (m), 6.32 (s), 8.48 τ (s), ratio: 4:3:6 (calculated ratio: 4:3:6).

Satisfactory analysis could not be obtained for this compound.

Lithium perchlorate

Lithium perchlorate trihydrate (67) was quantitatively dehydrated in a drying pistol with phosphorous pentoxide.

Tetrabutylammonium bromide

1-Bromobutane (137 g., 1 mole) and tributylamine (185 g., 1 mole) were heated in a 500 ml. round bottom flask on the steam bath for 10 days. The dark-red oil was recrystallized three times from ethyl acetate to give 179 g. (56%) of white crystals; m.p. 102.5-104.0° (reported (68) m.p. 102.7-103.5°).

Tetrabutylammonium perchlorate

Silver nitrate (55 g., .323 mole) was dissolved in 300 ml. of water, and 30% potassium hydroxide solution was added until the solution became strongly basic. The resultant black precipitate was washed by decantation with distilled water until it was neutral to litmus paper. The silver oxide was filtered and washed with a little cold water and ethanol. An 80.5 g. (.25 mole) quantity of tetrabutylammonium bromide was dissolved in 500 ml. of 60% ethanol, the freshly prepared silver oxide added, and the reaction mixture stirred overnight in the dark. When the solution tested negative to halide ion, the silver salt was filtered off, and 70% perchloric acid added to the solution until it was strongly acidic to litmus paper. Precipitation of the salt took place immediately. Recrystallization of the residue twice from ethyl acetate-pentane gave 77 g. (90%) of white crystals; m.p. 212.0-212.5° (reported (6) m.p. 212.0-212.5°).

Tetrabutylammonium azide

Tetrabutylammonium bromide (80.5 g., .25 mole) was dissolved in

200 ml. of 50% ethanol and stirred overnight with excess freshly prepared silver oxide. The silver halide was filtered off and the filtrate treated with excess hydrazoic acid until acidic to litmus paper. The pale-yellow solution was concentrated to 70 ml. and extracted three times with chloroform. Most of the chloroform was removed from the chloroform extracts at the aspirator. The flask containing the pale-yellow oil was placed in a vacuum dessicator, containing phosphorous pentoxide as dessicant, and evacuated until crystallization took place. The yellow solid obtained was recrystallized three times from purified ethyl acetate to give 63 g. (88%) of white, hygroscopic crystals which were stored in a vacuum dessicator using phosphorous pentoxide as dessicant. Infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly provided by D. Darwish.

Tetrabutylammonium 2,6-dimethylbenzenesulfinate

This compound was kindly donated by H. Persad.

Tetrabutylammonium 4-methylbenzenesulfinate

Tetrabutylammonium bromide (80.5 g., .25 mole) was dissolved in 200 ml. of 50% ethanol and treated overnight with excess silver oxide. The silver halide was filtered off and the solution carefully neutralized with *p*-toluenesulfinic acid (obtained from the sodium salt) until neutral to litmus paper. The yellow solution was concentrated at the aspirator to 75 ml. and extracted three times with chloroform. The chloroform was removed from the chloroform extracts at the aspirator and the residual oil was pumped at the vacuum pump until crystallization occurred. The yellow solid was recrystallized four times from ethyl acetate-ether to give 85 g. (80%) of

white, slightly hygroscopic needles. Infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly provided by D. Darwish.

KINETIC MEASUREMENTS

Procedure A

The arenesulfinate ester, 2,6-lutidine (and salt if used) were accurately weighed into a 100 ml. volumetric flask, which was filled to the mark with the appropriate solvent and mixed well. Aliquots of the solution were transferred with an automatic pipette into ca. 16 partially drawn-out test tubes, such that each contained in excess of 5.5 ml. The test tubes were sealed and placed into a basket in the appropriate constant temperature bath, one ampoule being retained as a "blank". After three minutes one ampoule was withdrawn for "zero point", the reaction being quenched by placing the ampoule into ice-water. At appropriate time intervals further ampoules were withdrawn and quenched. Three to four ampoules were reserved for infinity measurements and withdrawn from the bath after 10 half-lives or more for the reaction. After the ampoule had been equilibrated at 25°, it was opened and an aliquot removed by means of a 5 ml. calibrated automatic pipette, and delivered into a 60 ml. separatory funnel containing 25 ml. of pentane and 10 ml. of water. The separatory funnel was shaken vigorously 40 times, the aqueous layer drained and the pentane layer washed with a further 10 ml. of distilled water. The combined aqueous solutions were titrated with sodium methoxide to the pink end point of phenolphthalein, using 25 drops of indicator. The pentane layer was successively washed with 10 ml. of .1 N hydrochloric acid and three 10 ml.

portions of water and dried over anhydrous granular potassium carbonate. After drying, the solution was filtered into a 50 ml. pear-shaped flask and the pentane removed at the aspirator. The resultant residue was dissolved in 1 ml. of carbon tetrachloride, added by means of a calibrated pipette. The infrared spectrum of this solution was determined in a .5 mm. sodium chloride cell, on the Perkin Elmer Model 21 Spectrophotometer, using the 20 cm. per micron scale, and scanning from 1400-1250 cm^{-1} . A variable spacer reference cell, previously balanced against the sample cell, was used to compensate for any small absorbance due to the solvent.

The following expressions were used to calculate the first-order rate constants:

Rates measured by titrimetry:

$$k = \frac{2.303}{t} \log \frac{(T_{\infty} - T_0)}{(T_{\infty} - T)} \quad \text{where } T = \text{the titer at time } t.$$

Rates measured by infrared spectrophotometry:

$$k = \frac{2.303}{t} \log \frac{(D_{\infty} - D_0)}{(D_{\infty} - D)} \quad \text{where } D = \text{optical density at time } t.$$

Procedure B

This procedure was employed in all runs using 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate. It was also used in a number of runs on the other arenesulfinate esters. The detection of the end point is significantly better in this procedure than in the one previously described.

The arenesulfinate ester, 2,6-lutidine (and salt if used) were accurately weighed into a 50 ml. volumetric flask, which was filled to the

mark with anhydrous ethanol, previously equilibrated to 0 or 25°. The flask was vigorously shaken, while being held in the constant temperature bath, to effect rapid solution. Aliquots were removed at appropriate time intervals with a 5 ml. calibrated automatic pipette, and delivered into a 25 ml. Erlenmeyer flask, cooled in methanol-ice. The temperature of the cooling solution was not allowed to exceed -12°. The solution was titrated, while in the cooling bath, with sodium methoxide to the green end point of p-naphtholbenzein. The indicator was a .1% solution in anhydrous ethanol. "Infinity points" after titration were extracted as described in Procedure A above, to determine the amount of sulfone. Titrimetric first-order rate constants were calculated as above.

Procedure C

2-p-Nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate, .7146 g. (.02143 M), was weighed into a 100 ml. volumetric flask which was filled to the mark with anhydrous acetic acid, .0560 M in sodium acetate. The flask was shaken vigorously, and aliquots of the solution were distributed to 16 partially drawn out test tubes, such that each contained in excess of 5.5 ml. The test tubes were sealed, and the ampoules were placed into a basket which was immersed in the 90° constant temperature bath. After three minutes, three ampoules were withdrawn for use as "zero points". At appropriate time intervals, further sets of three ampoules were withdrawn from the bath, and placed into an ice-water bath. Each set of three ampoules was equilibrated at 25°, opened, and 5 ml. aliquots removed by means of a calibrated automatic pipette and delivered into a 250 ml. separatory funnel, containing 75 ml. of pentane and 30 ml. of distilled water. The separatory funnel was shaken 40 times, the aqueous layer

discarded, and the process repeated four times. The pentane layer was dried over anhydrous granular potassium carbonate. The solution was filtered into a 50 ml. pear-shaped flask and the pentane removed at the aspirator.

A standard solution of ethylene carbonate in chloroform (ethanol free) was prepared by dissolving .2389 g. of the compound in 10 ml. of the solvent. Aliquots (0.5 ml.) of this solution were added to each of the above "flasks", and the n.m.r. spectrum of the mixture recorded on the Varian Model A-60 Analytical Spectrophotometer. The rate of ester disappearance was followed by measurement of the band due to the aromatic methyl groups of the ester at 7.40 τ in chloroform. From the ratio of the integrated areas of the sample to internal standard, ethylene carbonate, the first-order rate constant was calculated by means of the following relationship:

$$k = \frac{2.303}{t} \log \frac{A_0}{A}$$

where A is the area ratio of the ester to ethylene carbonate at time t.

In the solvolysis of the above arenesulfinate ester in anhydrous ethanol, the same general procedure, with the following exceptions. For each "kinetic point" five ampoules were removed from the bath, and in the extraction procedure ether instead of pentane was used. The n.m.r. spectra were recorded on the HR 100 instrument.

Gas Chromatography

A Perkin Elmer Model 154D Vapor Fractometer was used for the product analyses on the various systems. The same general procedure was followed in all cases, changes were made only in the column used and the operating temperature.

2-Phenyl-2-propyl system

A series of standards containing various amounts of 2-phenylpropene, 2-phenyl-2-propyl ethyl ether and acetophenone were prepared, mixed, and 1-2 μ l. aliquots analyzed in triplicate. Column R (Ucon Oil 550) at a column temperature of 170°, and a helium pressure of 25 p.s.i. (gauge) was used. The average area ratio of olefin to acetophenone, and ether to acetophenone was calculated and plotted against the respective mole ratios. The results are given in Table X and Figure VII.

2-p-Tolyl-2-propyl system

A series of standards containing various amounts of 2-p-tolylpropene, 2-p-tolyl-2-propyl ethyl ether and acetophenone were prepared, mixed and 1-2 μ l. aliquots analyzed in duplicate. Column K (Carbowax 1500) at a column temperature of 140°, with a helium pressure of 25 p.s.i. (gauge) was used. The average area ratio of olefin to acetophenone, and ether to acetophenone was calculated and plotted against the respective mole ratios. These results are given in Table XXXII and Figure XV.

2-p-Bromophenyl-2-propyl system

A series of standards containing various amounts of 2-p-bromophenylpropene, 2-p-bromophenyl-2-propyl ethyl ether and acetophenone were prepared, mixed, and 1-2 μ l. aliquots analyzed in duplicate. Column K (Carbowax 1500) at a temperature of 174°, and a helium pressure of 25 p.s.i. (gauge) was used. The average area ratio of olefin to acetophenone, and ether to acetophenone was plotted against the respective mole ratios. The results are given in Table XXX and Figure XIV.

Control on the isolation of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, 2-phenylpropene, and 2-phenyl-2-propyl ethyl ether in anhydrous ethanol at 90° with added 2,6-lutidine. (Run I-238).

2-Phenyl-2-propyl 2,6-dimethylphenyl sulfone, .0622 g. (.002156 M), 2-phenyl-2-propyl ethyl ether, .1816 g. (.01107 M), 2-phenylpropene, .0866 g. (.00751 M), and 2,6-lutidine, .4728 g. (.04412 M), were weighed into a 100 ml. volumetric flask, which was filled to the 98 ml. mark (determined previously) with anhydrous ethanol. (The 98 ml. mark of the volumetric flask was found by filling the flask to the mark with 98% ethanol at 25°, and withdrawing 2 ml. of solvent by means of a 2 ml. measuring pipette.) The solution was transferred to a 160 ml. pressure bottle, the volumetric flask rinsed twice with 1 ml. portions of anhydrous ethanol and the rinsings added into the pressure bottle. The pressure bottle was placed into the 90° constant temperature bath and heated for 12 hours (ca. 12 half-lives for the reaction of the ester). After cooling to room temperature, the contents of the flask were poured into a 1 l. separatory funnel containing 450 ml. of pentane and 200 ml. of water. The pressure bottle was rinsed twice with 25 ml. of pentane, and the washings also added into the separatory funnel. After extraction, the aqueous layer was discarded. The pentane layer was washed twice with 75 ml. portions of water, twice with 50 ml. portions of .1 N hydrochloric acid, followed by three further washings with 50 ml. portions of distilled water. The pentane solution was dried over anhydrous granular potassium carbonate, and most of the solvent carefully removed by slow distillation through two 9" Vigreux columns, which were allowed to drain back into the flask when the distillation was over. The resultant solution was chromatographed on 30 g. of alumina, and eluted with 750 ml.

of pentane, followed by 500 ml. of 15% ether-pentane. The pentane fraction was once more carefully distilled through two 9" Vigreux columns to remove most of the solvent, and .0142 g. (.00183 mole) acetophenone was added. This solution was analyzed in triplicate, using a 2 meter Column R (Ucon Oil 550) on the Perkin Elmer Vapor Fractometer 154D at 170°. From the area ratio of olefin to acetophenone, and ether to acetophenone, the mole ratio and thus the number of moles of each compound was calculated by use of the calibration curve, and these are shown in Table XI.

From the second fraction obtained in chromatography (eluted with 15% ether-pentane), the solvent was removed by distillation and the resultant solid material recrystallized from pentane. The 62.2 mg. of crystalline material obtained, m.p. 152.1-152.9°, whose infrared and n.m.r. spectra and m.p. corresponded to authentic 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, (m.p. 152.5-153.0°), is equivalent to 97% of the original amount of sulfone.

Product run on 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° with added 2,6-lutidine. Run I-217.

2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate, .6425 g. (.02165 M), and 2,6-lutidine, .4835 g. (.04512 M), were weighed into a 100 ml. volumetric flask and treated exactly as described in the above control for the analysis of the products. The results obtained are listed in Table XII.

From the second fraction, obtained in chromatography on alumina, the solvent was removed at the aspirator, and the residue recrystallized from pentane. The 60.0 mg. of white needles obtained, m.p. 152.0-152.7°, whose infrared and n.m.r. spectra and m.p. corresponded to authentic 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone (m.p. 152.5-153.0°, page 151), is

equivalent to 9.6% based on starting 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate.

Product run on 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in 80% ethanol at 70° with added 2,6-lutidine. Run I-226.

2-Phenyl-2-propyl 2,6-dimethylbenzenesulfinate, .6286 g. (.02180 M), and 2,6-lutidine, .4966 g. (.04634 M), were weighed into a 100 ml. volumetric flask, which was filled to the 98 ml. mark with 80% ethanol. The solution was transferred into a 160 ml. pressure bottle, and the volumetric flask rinsed twice with 1 ml. portions of 80% ethanol and the rinsings were added to the pressure bottle. The pressure bottle was placed into the 70° constant temperature bath and heated for 9 hours (ca. 17 half-lives for the reaction of the ester). After cooling to room temperature, the contents of the flask were poured into a 1 l. separatory funnel containing 450 ml. of pentane and 200 ml. of water. The pressure bottle was rinsed twice with 25 ml. portions of pentane and the washings added into the separatory funnel. After extraction, the aqueous layer was discarded. The pentane layer was washed twice with 75 ml. portions of water, twice with 50 ml. portions of .1 N hydrochloric acid, followed by three further washings with 50 ml. portions of distilled water. The pentane solution was dried over anhydrous granular potassium carbonate, and most of the solvent was carefully removed by slow distillation through two 9" Vigreux columns, which were allowed to drain back into the flask when the distillation was over. The resultant solution was chromatographed on 30 g. of alumina, and eluted with 750 ml. of pentane, 850 ml. of 5% ether-pentane, followed by 500 ml. of 50% ether-pentane. The first fraction was once again carefully distilled through two 9" Vigreux columns to remove most of the solvent, and .0248 g.

(.00207 mole) of acetophenone added. This solution was analyzed in triplicate, using a 2 meter Column R (Ucon Oil 550) on the Perkin Elmer Vapor Fractometer 154D at 170°. From the area ratio of olefin to acetophenone, and ether to acetophenone, the mole ratio, and thus the number of moles of each compound was calculated by the use of the calibration curve, and these results are shown in Table XII.

From the second fraction obtained in chromatography (eluted with 5% ether-pentane), the solvent was removed by distillation, and the resultant solid material recrystallized from pentane. The 102 mg. of crystalline material obtained, m.p. 152-153°, whose infrared and n.m.r. spectra and m.p. corresponded to authentic 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone (m.p. 152.5-153.0°, page 151), is equivalent to 16.2% based on starting arenesulfinic acid ester.

Removal of the solvent from the last fraction gave 27 mg. of pale-yellow oil, whose infrared spectrum was superimposable upon that of an authentic sample of 2-phenyl-2-propanol. These results are summarized in Table XII.

Lambert Beer Law and extraction procedure control

The same general procedure was used to determine the relationship between optical density and concentration.

A solution of 2-phenyl-2-propyl 2,6-dimethylphenyl sulfone, .2533 g. (.008783 M) in 100 ml. of 98% ethanol was prepared. Using a calibrated, automatic pipette, 20, 15, 10 and 5 ml. portions of the solution were transferred to four 25 ml. volumetric flasks. These flasks were filled to the mark with 98% ethanol to give solutions of the concentrations listed in Table I. Five ml. aliquots of these solutions and the parent solution

were removed and extracted exactly as described in kinetic procedure A. The percentage transmittance at 1308 cm.^{-1} in carbon tetrachloride was measured. The optical density was plotted against the concentration as given in Figure II and Table I.

Control on the isolation of 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone, 2-p-bromophenylpropene and 2-p-bromophenyl-2-propyl ethyl ether in anhydrous ethanol at 90° with added 2,6-lutidine. Run III-1.

2-p-Bromophenyl-2-propyl 2,6-dimethylphenyl sulfone, .0732 g. (.00199 M), 2-p-bromophenyl-2-propyl ethyl ether, .2291 g. (.00943 M), 2-p-bromophenylpropene, .1700 g. (.00863 M), and 2,6-lutidine, .4860 g. (.04535 M) were weighed into a 100 ml. volumetric flask, which was filled to the 98 ml. mark (determined previously) with anhydrous ethanol. The solution was transferred to a 160 ml. pressure bottle, the volumetric flask rinsed twice with 1 ml. portions of anhydrous ethanol, and the rinsings added into the pressure bottle. The pressure bottle was immersed in the 90° constant temperature bath for 33 hours (11 half-lives for the reaction of the arenesulfinate ester). Subsequent treatment was exactly as described for the unsubstituted system, except in gas chromatography, Column K at 174° was used. The results are listed in Table XXXI.

From the fraction containing the sulfone, the solvent was removed by distillation, and the residue recrystallized from pentane. The 71.5 mg. of crystalline material, m.p. 147.8-148.1°, whose infrared and n.m.r. spectra and m.p. corresponded to authentic 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone (m.p. 148.7-149.0°, page 152), is equivalent to 97.5% of the original amount of sulfone.

Product run on 2-p-bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° with added 2,6-lutidine. Run III-5.

2-p-Bromophenyl-2-propyl 2,6-dimethylbenzenesulfinate, .7713 g. (.02100 M) and 2,6-lutidine, .4785 g. (.04465 M), were weighed into a 100 ml. volumetric flask and treated exactly as described in the above control isolation of the products. Analysis by gas chromatography showed the presence of 41.8% 2-p-bromophenylpropene and 48.7% 2-p-bromophenyl-2-propyl ethyl ether. The 64.5 mg. of 2-p-bromophenyl-2-propyl 2,6-dimethylphenyl sulfone, m.p. 148.2-148.5°, obtained, corresponded to 8.4% based on starting ester. Its infrared and n.m.r. spectra and m.p. were identical to authentic sulfone (m.p. 149.7-149.0°, page 152).

Control isolation of 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone.

2-p-tolylpropene and 2-p-tolyl-2-propyl ethyl ether in anhydrous ethanol at 90° with added 2,6-lutidine. Run III-13.

2-p-Tolyl-2-propyl 2,6-dimethylphenyl sulfone, .0573 g. (.00189 M), 2-p-tolyl-2-propyl ethyl ether, .2012 g. (.01130 M), 2-p-tolylpropene, .1566 g. (.01186 M), and 2,6-lutidine, .5101 g. (.04760 M), were weighed into a 100 ml. volumetric flask which was filled to the 98 ml. mark (previously determined) with anhydrous ethanol. The solution was transferred to a 160 ml. pressure bottle, the volumetric flask rinsed twice with 1 ml. portions of anhydrous ethanol, and the rinsings added into the pressure bottle. The pressure bottle was immersed in the 90° constant temperature bath for 70 minutes (25 half-lives for the reaction of the corresponding ester). Subsequent treatment was exactly as described for the unsubstituted system, except in gas chromatography Column K at 140° was used. The results are listed in Table XXXIII.

From the fraction containing the sulfone, the solvent was removed by distillation, and the residue recrystallized from pentane. The 56.5 mg. of white needles, m.p. 138.7-139.2°, whose infrared and n.m.r. spectra and m.p. corresponded to authentic sulfone (m.p. 139.5-140.0°, page 152), is equivalent to 99.0% of the original sulfone.

Product run on 2-p-tolyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90° with added 2,6-lutidine, Run III-16.

2-p-Tolyl-2-propyl 2,6-dimethylbenzenesulfinate, .6696 g. (.02214 M), and 2,6-lutidine, .4785 g. (.04423 M), were weighed into a 100 ml. volumetric flask and treated exactly as in the above control isolation of the products. Heating in the 90° constant temperature bath was carried out for 50 minutes only. Gas chromatographic analysis showed the presence of 30.3% 2-p-tolylpropene and 53.9% 2-p-tolyl-2-propyl ethyl ether. The 96.5 mg. of 2-p-tolyl-2-propyl 2,6-dimethylphenyl sulfone, m.p. 139.2-139.6°, corresponds to 14.4% based on starting ester. Its infrared and n.m.r. spectra and m.p. were identical to authentic sulfone (m.p. 139.5-140.0°, page 152).

Control on the isolation of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, 2-p-methoxyphenyl-2-propyl ethyl ether and 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone in anhydrous ethanol at 25° with added 2,6-lutidine. Run III-37.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, .0391 g. (.00246 M), 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone, .0034 g. (.00022 M), and 2-p-methoxyphenyl-2-propyl ethyl ether, .0912 g. (.00940 M), and 2,6-lutidine, .2412 g. (.04502 M), were weighed into a 50 ml. volumetric flask, which was filled to the mark with anhydrous ethanol. (Weighings

of less than 50 mg. were performed on a Mettler "Micro-gramatic" balance). The flask was shaken well, and immersed into the 25° constant temperature bath for one hour (ca. 11 half-lives for the reaction of the ester). The solution was poured into a 500 ml. separatory funnel, containing 250 ml. of methylene chloride and 100 ml. of water. The separatory funnel was shaken vigorously 40 times, and the aqueous layer discarded. The methylene chloride solution was washed twice with 25 ml. portions of .1 N hydrochloric acid, followed by three washings with distilled water. The organic layer was dried with anhydrous potassium carbonate, filtered and the solvent slowly distilled through two 9" Vigreux columns, which were allowed to drain back into the flask after the distillation was completed. A known amount of ethylene carbonate (internal standard) was added, and the n.m.r. spectrum recorded at 100 Mc. From the ratio of areas obtained, the percentage of each compound recovered was calculated. The results obtained are listed in Table XXXIV.

Product run on 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 25° with added 2,6-lutidine. Run III-42.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate, .3547 g. (.02228 M), and 2,6-lutidine, .2418 g. (.04513 M), were weighed into a 50 ml. volumetric flask, which was filled to the mark with anhydrous ethanol. The subsequent treatment was exactly as in the above control run. The results obtained are given in Table XXXV.

Control on the isolation of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, and 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone in anhydrous acetic acid at 25° in the presence of added sodium acetate. Run III-49.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone, .0345 g. (.00217 M), and 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone, .0062 g. (.00047 M), were weighed into a 50 ml. volumetric flask, which was filled to the mark with anhydrous acetic acid (.0560 M in sodium acetate). The flask was immersed in the 25° constant temperature bath for 40 minutes. The same workup was used as in the ethanolysis experiment (Run III-37). The n.m.r. spectrum was recorded at 100 Mc. in CDCl_3 . From the area ratio of component to internal standard, the amount of each sulfone was calculated. 90% 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone and 104% 2-p-methoxyphenyl-2-propyl 4-methylphenyl sulfone were recovered.

Product run on 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous acetic acid at 25° with added sodium acetate. Run III-44.

2-p-Methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinate, .1800 g. (.02261 M), was weighed into a 25 ml. volumetric flask, which filled to the mark with anhydrous acetic acid (.0560 M in sodium acetate). The subsequent workup was exactly as in control experiment (III-49) above. From the n.m.r. spectrum, the ratio of 2-p-methoxyphenyl-2-propyl 2,6-dimethylphenyl sulfone to ethylene carbonate was measured, and 27.8% of the sulfone was found.

SAMPLE RATE RUNS

TABLE XL

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02128 M)
IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04507 M). RUN-I-157.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.727 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.794	59,400	2.785
750	2.775	112,200	2.773
2,820	2.782	195,000	2.751
18,780	2.774	346,380	2.764

TABLE XLI

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02139 M)
IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04602 M). RUN II-197.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.781 ml.

Time (hrs.)	Titer (ml.)	Time (hrs.)	Titer (ml.)
0	2.782	319	2.989
0	2.784	926	2.967
58.5	2.779	1,016.5	2.90
128.5	2.785	1,984	2.92
177	2.802	2,776	2.96

TABLE XLII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02188 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE.
(.04492 M). RUN II-171.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.839 ml.

Time (hrs.)	Titer (ml.)	$\log \frac{I}{I_0}$ (a)	F _{sulfone}	$10^7 k$, sec. ⁻¹ titr.	i.r.
0	0.088	0.02816			
71	.132	.05461		(0.70)	(2.59)
227	.335	.06518	0.140	1.28	1.28
530.5	.607	.10517	.130	1.23	1.38
840	.884	.12287	.107	1.28	1.13
1,176	1.048	.14983	.108	1.15	1.13
1,699	1.486	.19839	.103	1.35	1.27
2,758	1.895	.24527	.099	1.31	1.20
4,056	2.243				
Infinity ^(b)	2.573	.33726	.100		
Average:				1.28 ±.06	1.23 ±.08

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Two ampoules, which were kept in the 25° constant temperature bath for 4,056 hours, were placed into the 90° bath for 10 hours (12 half-lives for the reaction of 2-phenyl-2-propyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90°).

% Infinity Titer: 90.5. % Sulfone at infinity: 10.2.

TABLE XLIII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02198 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04378 M) RUN II-69,70.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.820 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k$, sec. ⁻¹ titr.	i.e.
Blank	0.053			
0	.095	0.01828		
240(b)	.209	.03383		2.29
480	.332	.04766	2.27	2.22
780	.478	.06333	2.18	2.16
1,080	.625	.08314	2.24	2.34
1,440	.773	.09726	2.21	2.20
1,920	.958	.11461	2.20	2.10
2,700	1.210	.14644	2.17	2.16
3,600	1.495	.17609	2.25	2.18
4,500	1.667	.20003	2.16	2.19
6,000	1.945	.23426	2.19	2.27
8,700	2.273	.26316	2.26	2.13
10,800	2.420		2.31	
36,000	2.627			
36,000	2.632	.30878		
39,600	2.636			
			Average: $2.22 \pm .04$	$2.20 \pm .06$

(a) Absorbance at 1308 cm^{-1} in CCl_4 .

(b) Considered as zero time for titrimetric rate calculations.

% Infinity titer: 91.4.

% Sulfone at infinity: 9.2.

TABLE XLIV

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02198 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.09340 M). RUN I-223,224.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.816 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I}{I_0}$ (a)	$10^4 k$, sec. ⁻¹ titr.	i.r.
Blank	0.041			
0	.118	0.01703		
360(b)	.283	.02653		
660	.420	.03941	2.02	1.99
960	.562	.05077	2.13	1.92
1,500	.795	.07518	2.18	2.16
2,100	.986	.09272	2.06	2.03
2,700	1.208	.10755	2.16	1.93
3,600	1.441	.13862	2.12	2.16
4,500	1.643	.15381	2.12	2.05
5,400	1.816	.18355	2.13	2.42
7,200	2.065	.19756	2.12	2.13
9,000	2.242	.22037	2.13	2.36
46,800	2.608			
52,500	2.616	.24944		
52,500	2.616			
			Average: $2.12 \pm .03$	$2.12 \pm .13$

(a) Absorbance at 1308 cm^{-1} in CCl_4 .

(b) Considered as zero time for rate calculations.

% Infinity titer: 91.4.

% Sulfone at infinity: 9.8.

TABLE XLV

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02217 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-DIMETHYL-
BENZENESULFINIC ACID (.01957 M) AND 2,6-LUTIDINE (.09354 M).
RUN I-219,220.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.840 + 2.508

= 5.348 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	2.608			
0	2.660	0.00860		
360(b)	2.751	.01995		
660	2.925	.03663	2.46	2.53
1,140	3.176	.06333	2.44	2.71
1,740	3.450	.08991	2.43	2.67
2,700	3.833	.11959	2.49	2.47
3,600	4.113	.14953	2.50	2.61
5,400	4.457	.18213	(2.31)	2.48
9,000	4.908	.23223	2.45	(3.16)
46,800	5.209			
57,600	5.195	.24699		
			Average: $2.46 \pm .02$	$2.58 \pm .09$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .

(b) Considered as zero time for rate calculations.

% Infinity titer: 91.3.

% Sulfone at infinity: 9.6.

TABLE XLVI

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02140 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04822 M) AND LITHIUM PERCHLORATE (.03401 M). RUN I-189,190.

Base: NaOCH₃ (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.742 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I}{I^0}$ (a)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.078			
0	.132	0.01494		
240	.286		2.72	
540	.471	.04571	2.78	2.77
900	.692	.06221	2.90	2.66
1,320	.898	.06670	2.86	(2.01)
1,800	1.121	.10278	2.89	2.80
2,280	1.316	.11461	2.90	2.62
2,880	1.483	.13545	2.81	2.72
3,600	1.679	.17609	2.80	(3.59)
5,400	2.075	.19257	2.96	2.98
7,200	2.274	.21352	2.93	3.12
36,000	2.565			
77,600	2.569	.23704		
77,600	2.562			
			Average: 2.85 ± .05	2.81 ± .13

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.
% Infinity titer: 90.8. % Sulfone at infinity: 9.6.

TABLE XLVII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02226 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04673 M) AND TETRABUTYLAMMONIUM PERCHLORATE (.03848 M). RUN-II-73,74.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.853 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k$, sec. ⁻¹ titr.	i.r.
Blank	0.052	0.00000		
0	.092	0.01368		
600	.424	.05231	2.34	2.44
960	.608	.07115	2.37	2.36
1,440	.809	.09096	2.31	2.21
1,920	1.007	.11361	2.33	2.26
2,400	1.183	.14114	2.35	2.49
3,000	1.385	.16167	2.38	2.46
3,600	1.512	.16673	2.28	2.16
4,500	1.745	.20303	2.35	2.44
5,700	1.959	.22324	2.34	2.36
7,800	2.212	.25527	2.32	2.45
9,600	2.370	.26007	2.39	(2.12)
39,600	2.616			
39,600	2.628	.29710		
43,200	2.635			

Average: $2.34 \pm .02$

$2.36 \pm .09$

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

% Infinity titer: 90.8.

% Sulfone at infinity: 8.5.

TABLE XLVIII

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID
(.02040 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04621 M) AND TETRABUTYLAMMONIUM PERCHLORATE (.08334 M). RUN II-129.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.650 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.643	18,600	2.670
1,800	2.646	36,000	2.705
3,600	2.662	86,400	2.729
7,200	2.652	172,800	2.709

TABLE XLIX

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02157 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED TETRABUTYLAMMONIUM
BROMIDE (.03342 M) AND 2,6-LUTIDINE (.04191 M). RUN II-124.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.799 ml.

Time (sec.)	Titer (ml.)	Corrected Titer(ml.)(a)	$\log \frac{I_0}{I}$ (b)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.086				
0	.161	0.161	0.01494		
360(c)	.339	.339	.03623		2.30
600	.462	.462	.04999	2.37	2.33
960	.608	.608	.06781	(2.15)	2.28
1,440	.819	.819	.09795	2.25	2.56
1,920	1.008	1.008	.11826	2.29	2.53
2,460	1.187	1.187	.14082	2.29	2.54
3,000	1.329	1.329	.16047	2.24	2.60
3,600	1.503	1.503	.17840	2.29	2.57
4,500	1.714	1.714	.19005	2.33	2.34
5,700	1.905	1.905	.21696	2.28	2.44
7,200	2.093+.050	2.143	.24214	2.31	2.59
43,200	2.372+.200	2.572			
43,200	2.356+.200	2.556	.28375		
86,400	2.209+.360	2.569			

Average: 2.29±.03 2.46±.11

(a) Corrections added, based on Run II-125. (b) Absorbance at 1308 cm.⁻¹
in CCl₄. (c) Considered as zero time for rate calculations.
% Infinity titer: uncorrected 81.5; corrected 88.6. % Sulfone at infinity: 8.5.

TABLE I

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02139 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED TETRABUTYLAMMONIUM
BROMIDE (.07169 M) AND 2,6-LUTIDINE (.04418 M). RUN II-143,144.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.775 ml.

Time (sec.)	Titer (ml.)	Corrected Titer(ml.)(a)	$\log \frac{I_0}{I}$ (b)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.042				
0	.130	0.130	0.01912		
450	.387	.387	.04571	2.49	2.34
600	.457	.457	.05538	2.41	2.44
900	.596	.596	.07004	2.37	2.36
1,320	.781	.781	.09272	2.37	2.45
1,800	.955	.955	.11826	2.31	2.58
2,100	1.097	1.097		2.42	
3,300	1.485	1.485	.16554	2.48	2.42
4,500	1.626+.080	1.706	.19893	2.33	2.50
6,000	1.875+.100	1.975	.22994	2.38	2.61
33,840	2.326+.232	2.558			
33,840	2.322+.232	2.554	.28533		
82,800	2.097				
Average:				2.40+.05	2.46+.08

(a) Corrections added, based on Run II-145.

(b) Absorbance at 1308 cm.⁻¹ in CCl₄.

% Infinity titer: uncorrected 83.5; corrected 90.5. % Sulfone at infinity: 8.6.

TABLE LI

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02048 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04571 M) AND TETRABUTYLAMMONIUM BROMIDE (.03594 M). RUN II- 125.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.657 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.662	14,400	2.621
0	2.652	24,300	2.553
0	2.667	43,200	2.460
900	2.655	82,800	2.303
1,980	2.647	129,600	2.112
3,300	2.623	183,600	1.990
4,800	2.621	259,200	1.682
7,200	2.614	518,400	1.480

TABLE LII

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02155 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04535 M) AND TETRABUTYLAMMONIUM BROMIDE (.07004 M). RUN II-145.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.796 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.745	6,000	2.651
0	2.749	26,400	2.515
1,440	2.714	33,840	2.458
3,600	2.678	82,800	2.104

TABLE LIII

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02019 M)
IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04481 M) AND
POTASSIUM THIOCYANATE (.03578 M). RUN II-131.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.619 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.162	14,400	2.132
600	2.296	21,600	2.125
1,440	2.246	36,000	2.091
2,400	1.924	79,200	1.775
3,600	1.914	93,600	1.862
4,320	2.233	126,000	1.791
5,400	2.243	264,600	1.536
7,200	2.186	360,000	1.485

TABLE LIV

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02181 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED POTASSIUM THIOCYANATE (.01810 M) AND 2,6-LUTIDINE (.04397 M). RUN II-120.

Aliquot: 5.046 ml.

Time (sec.)	$\log \frac{I_0}{I} (a)$	$10^4 k, \text{sec.}^{-1}$
0	0.03060	
960(b)	.07445	
1,440	.10346	3.07
1,920	.12320	2.72
2,400	.14082	2.61
3,000	.16435	2.71
3,660	.19201	2.99
4,500	.21005	2.88
5,400	.22763	2.88
6,660	.24773	2.98
64,800	.28646	
75,600		
Average:		$2.85 \pm .13$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .

(b) Considered as zero time for rate calculations.

% Sulfone at infinity: 8.5.

TABLE LV

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02176 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04440 M) AND TETRABUTYLAMMONIUM AZIDE (.0818 M), RUN II-179,180.

Base: NaOCH₃ (.03888 M),

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.823 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k$, sec. ⁻¹ titr.	i.r.
Blank	0.076			
0	.098	0.02531		
240	.272	.03503	2.43	
420	.304	.04805	2.36	
600(b)	.389	.05115	2.38	
840	.482	.06446	2.30	2.19
1,080	.591	.07918	2.37	2.37
1,380	.675	.09237	2.22	2.22
1,680	.815	.10653	2.45	2.22
2,100	.940	.12320	2.31	2.16
2,700	1.090	.14644	2.24	2.17
3,600	1.347	.16732	2.35	1.97
4,500	1.504	.21299	2.29	2.50
5,400	1.634	.23578	2.25	2.53
34,200	2.280			
60,300	2.288	.28521		
78,300	2.284			

Average: 2.33_±.06 2.26_±.14

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for infrared rate calculations.

% Infinity titer: 78.2. % Sulfone at infinity: 8.7.

TABLE LVI

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02176 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04440 M) AND TETRABUTYLAMMONIUM AZIDE (.0818 M). RUN II-181.

Aliquot: 5.046 ml.

Time (sec.)	$\log \frac{I_0}{I}(a)$	Conc., $10^3 M$	$10^4 k, \text{sec.}^{-1}$
0	0.00000	0.00	
420(b)	.01953	0.82	
840	.03423	0.95	1.75
1,380	.05308	1.15	2.06
2,100	.07591	1.40	2.27
3,600	.11959	1.83	2.51
5,400	.14891	2.10	2.40
34,200	.20412	2.65	
60,300			
Average:			$2.20 \pm .23$

(a) Absorbance at 2100 cm.^{-1} in CCl_4 .

(b) Considered as zero time for rate calculations.

% 2-Phenyl-2-propyl azide at infinity: 12.2.

TABLE LVII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02239 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04242 M) AND TETRABUTYLAMMONIUM AZIDE (.2847 M). RUN III-38.

Base: NaOCH_3 (.03888 M)

Aliquot: 5.046 ml.

Indicator: p-Naphtholbenzein.

Calculated infinity: 2.904 ml.

Time (sec.)	Titer (ml.)	$10^4 k, \text{sec.}^{-1}$
Blank	0.000	
0	.000	
600	.272	2.73
1,200	.501	2.72
1,800	.720	2.84
2,400	.896	2.87
3,600	1.143	2.80
7,200	1.576	2.89
36,000	1.796	
36,000	1.806	

Average: $2.81 \pm .06$

% Infinity titer: 62.0.

TABLE LVIII

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02096 M)
IN 80% ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE (.04623 M). RUN I-153.

Base: NaOCH_3 (.03847 M)

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 2.716 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.668	65,640	2.697
1,260	2.667	167,940	2.684
3,600	2.642	257,640	2.692
37,560	2.674		

TABLE LIX

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02155 M) IN 80% ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE (.09233 M).
RUN I-103,104.

Base: NaOCH₃ (.03847 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.791 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I}{I^0}$ (a)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.035			
0	.064	0.02449		
180(b)	.168			
300	.257	.06483	3.56	3.69
540	.392	.08672	(3.09)	3.27
900	.650	.12581	3.57	3.39
1,200	.830	.15229	3.66	3.69
1,500	.988	.17522	3.69	3.34
1,920	1.150	.20412	3.56	3.42
2,400	1.352	.23955	3.67	3.41
2,880	1.501	.27346	3.65	3.61
3,600	1.684	.27669	3.65	(2.96)
4,500	1.880	.31471	3.79	3.11
5,400	2.016	.37181	(3.94)	(4.29)
7,200	2.140	.37585	3.74	3.39
42,660	2.294	.40943		
Average:			3.65 \pm .11	3.43 \pm .14

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for rate calculations.

% Infinity titer: 81.0. % Sulfone at infinity: 16.5.

TABLE LX

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02151 M) IN 80% ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE (.09149 M)
AND 2,6-DIMETHYLBENZENESULFINIC ACID (.02726 M). RUN I-99,100.

Base: NaOCH₃ (.03847 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.786 + 3.531

= 6.317 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k$, sec. ⁻¹ titr.	i.r.
Blank	3.540			
0	3.613	0.02612		
180(b)	3.725	.04258		
300	3.814	.05918	3.53	3.84
540	3.944	.08422	(2.99)	3.35
900	4.195	.12189	3.43	(4.39)
1,200	4.376	.15045	3.54	3.41
1,500	4.542	.16613	3.63	3.12
1,920	4.698	.20412	3.47	3.21
2,400	4.879	.22994	3.48	3.22
2,880	5.020	.25600	3.43	3.23
3,600	5.225	.28981	3.51	3.28
4,500	5.407	.33264	3.55	3.62
5,400	5.558	.36418	3.68	4.01
7,200	5.677	.37639	3.42	3.94
42,720	5.871	.40943		
Average:			3.52± .07	3.47± .27

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for infrared rate calculations.

% Infinity titer: 83.5. % Sulfone at infinity: 16.5.

TABLE LXI

CONTROL ON THE STABILITY OF 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE
(.04550 M). RUN I-233.

Base: NaOCH₃ (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	0.150	25,680	0.217
600	.151	47,100	.230
1,680	.146	87,840	.224
3,960	.173	216,240	.242
10,800	.183		

TABLE LXII

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.02349 M)
IN 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.04869 M). RUN I-159.

Base: NaOCH₃ (.03888M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 3.011 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	3.076	25,680	3.165
600	3.092	47,100	3.160
1,680	3.105	87,840	3.246
3,960	3.114	216,240	3.345
10,800	3.140		

TABLE LXIII

CONTROL ON THE STABILITY OF 90% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE
(.02158 M). RUN I-241.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	0.084	208,800	0.146
6,300	.096	252,000	.164
32,700	.109	293,400	.192
46,800	.112	349,200	.198
102,000	.158	435,600	.172
130,500	.175	572,400	.153
166,200	.164	691,200	.147

TABLE LXIV

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.01059 M)
IN 90% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.02136 M). RUN I-243.

Base: NaOCH_3 (.03888 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 1.356 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	1.403	166,200	1.525
6,300	1.436	208,800	1.534
18,000	1.439	252,000	1.549
32,700	1.446	293,400	1.554
46,800	1.470	349,200	1.562
75,900	1.478	435,600	1.576
102,000	1.475	572,400	1.595
130,500	1.485	691,200	1.604

TABLE LXV

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02136 M) IN 90% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.04672 M).
RUN I-113,114.

Base: NaOCH₃ (.03847 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.767 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^5 k, \text{sec.}^{-1}$ titr.	i.r.
Blank	0.072			
0	.094	0.00945		
1,800(b)	.260	.02078		2.45
3,900	.384	.03181	2.49	2.28
6,300	.492	.04454	2.20	2.28
8,100	.572	.05115	2.18	2.16
9,900	.650	.05956	2.15	2.14
12,300	.775	.08707	2.26	(2.86)
16,980	.930	.08814	2.12	2.11
24,540	1.290	.10619	2.41	(1.87)
29,280	1.417	.14983	2.34	2.62
37,800	1.538		2.07	
50,105	1.814	.18213	2.10	2.15
68,340	2.093		2.10	
105,180	2.487		2.37	
457,200	2.685			
		.27138		
457,200	2.707			
Average:			2.23 \pm .12	2.27 \pm .13

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for titrimetric rate calculations.

% Infinity titer: 94.8. % Sulfone at infinity: 11.0.

TABLE LXVI

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02230 M) IN 90% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.09369 M)
AND 2,6-DIMETHYLBENZENESULFINIC ACID (.02605 M). RUN I-117,118.

Base: NaOCH_3 (.03847 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.888 + 3.375

= 6.263 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I}{I_0}$ (a)	$10^5 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	3.430			
0	3.450	0.00945		
1,800	3.562	.01284	2.32	2.00
3,600	3.649	.02490	2.10	(1.66)
7,200	3.848	.03703	2.19	(1.53)
10,800	3.994	.06221	2.06	2.05
15,300	4.210	.07882	2.13	1.98
19,800	4.378	.09968	2.10	2.10
24,300	4.583	.11361	2.23	2.05
30,600	4.813	.13704	2.26	2.14
38,400	4.981	.16346	2.14	2.26
48,600	5.228	.18327	2.16	2.19
57,600	5.419	.21059	2.21	(2.46)
86,400	5.780	.24030	2.22	2.36
106,200	5.946	.25479	2.30	(3.07)
277,200	6.174	.27485		
352,800	6.192			
Average:			2.19 ± .07	2.13 ± .10

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
% Infinity titer: 95.3. % Sulfone at infinity: 10.5.

TABLE LXVII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02191 M) IN 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.04475 M).
RUN I-141,142.

Base: NaOCH₃ (.03847 M)

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.838 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k, \text{sec.}^{-1}$ titr.	i.r.
Blank	0.106			
0	0.146	0.01536		
300(b)	.244	.03060	(1.42)	
720	.365	.06258	(1.36)	1.78
1,200	.571	.09587	1.66	1.77
1,800	.750	.13226	1.65	1.74
2,520	.955	.16761	1.67	1.67
3,300	1.173	.20548	1.74	1.67
4,200	1.352	.24576	1.71	1.70
5,100	1.518	.29951	1.71	(1.94)
6,000	1.671	.33203	1.74	(2.00)
7,200	1.851		1.79	
9,600	2.063	.38917	1.75	1.78
10,800	2.147	.41162	1.77	(1.87)
14,400	2.304	.43648	1.72	1.75
61,200	2.497	.47392		
61,200	2.504			
Average:			1.72 \pm .04	1.73 \pm .04

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for infrared rate calculations.

% Infinity titer: 84.2. % Sulfone at infinity: 18.7.

TABLE LXVIII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02188 M) IN 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.09635 M) AND 2,6-DIMETHYLBENZENESULFINIC ACID (.02403 M). RUN I-145,146.

Base: NaOCH₃ (.03847 M).

Aliquot: 4.983 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.834 + 3.113

= 5.947 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k$, sec. ⁻¹ titre	i.r.
Blank	3.134			
0	3.167	0.01536		
300	3.207	.03383	(0.56)	(1.50)
720	3.454	.06744	1.79	1.84
1,200	3.602	.09377	1.69	1.73
1,800	3.795	.13513	1.71	1.87
2,520	3.991	.17840	1.69	1.95
3,300	4.211	.21880	1.76	2.01
4,200	4.388	.25382	1.72	1.77
5,100	4.589	.29623	1.79	(2.17)
6,000	4.707	.30298	1.75	1.93
7,200	4.858	.33586	1.73	2.00
9,000	5.064	.34655	1.79	1.73
11,100	5.211	.36380	1.78	1.73
14,400	5.332	.39164	1.69	1.57
88,560	5.552	.43521		
88,560	5.556			
Average:			1.74± .04	1.83± .11

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

% Infinity titer: 84.9. % Sulfone at infinity: 17.2.

TABLE LXIX

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02182 M) IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM
ACETATE (.05600 M). RUN II-91.

Aliquot: 4.983 ml.

Time (sec.)	$\log \frac{I_0}{I} \text{ (a)}$	$10^6 k, \text{ sec.}^{-1}$
0	0.01912	
18,000	.08027	4.18
30,600	.12678	4.42
41,400	.15381	4.20
72,000	.24993	4.42
100,800	.31931	4.37
136,800	.37621	4.03
170,100	.43632	4.01
210,600	.48686	3.84
266,400	.48855	(3.06)
288,000	.59627	4.01
338,400	.63357	3.85
338,400	.65263	4.11
511 hrs.		
	.86250	
557 hrs.		
		Average: 4.13± .17

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
% Sulfone at infinity: 26.3.

TABLE LXX

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02164 M) IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM
ACETATE (.11200 M). RUN II-43.

Aliquot: 4.983 ml.

Time (sec.)	$\log \frac{I_0}{I} (a)$	$10^6 k, \text{ sec.}^{-1}$
0	0.02979	
5,400	.03902	(1.89)
12,600	.08707	(5.17)
36,600	.15594	4.08
64,200	.25237	4.38
73,200	.27967	4.40
90,900	.33465	4.50
133,200	.42878	4.34
155,700	.46150	4.14
175,500	.50474	4.22
210,600	.55449	4.09
238,800	.62706	4.49
504 hrs.	.88553	
552 hrs.		
Average:		$4.29 \pm .14$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
% Sulfone at infinity: 26.4.

TABLE LXXI

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02151 M) IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM ACETATE (.05600 M) AND LITHIUM PERCHLORATE (.02426 M). RUN II-39.

Aliquot: 4.983 ml.

Time (sec.)	$\log \frac{I_0}{I} \text{ (a)}$	$10^6 k, \text{sec.}^{-1}$
0	0.02243	
3,000	.03623	7.85
6,300	.05652	9.39
14,400	.09447	8.98
28,800	.13925	7.61
40,500	.18270	7.77
54,600	.24155	8.44
81,900	.31302	8.21
92,700	.33041	7.89
108,900	.37346	8.22
129,600	.39881	7.76
144,900	.41681	7.53
170,100	.46776	8.15
552 hrs.	.61614	
576 hrs.		

Average: $8.15 \pm .42$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
% Sulfone at infinity: 17.4.

TABLE LXXII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02197 M) IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM
ACETATE (.05600 M) AND TETRABUTYLAMMONIUM PERCHLORATE (.07066 M).
RUN II-87.

Aliquot: 4.983 ml.

Time (sec.)	$\log \frac{I_0}{I}$ (a)	$10^6 k, \text{ sec.}^{-1}$
0	0.02449	
7,200(b)	.05385	
14,400	.08600	7.48
23,400	.12516	7.65
39,000	.19201	8.04
54,000	.23096	7.30
91,800	.32838	7.04
107,400	.38238	7.68
122,400	.41880	7.87
152,400	.45652	7.39
180,000	.49803	7.52
207,900	.56265	(8.88)
207,900	.54864	8.24
295 hrs.		
	.66586	
315 hrs.		
Average:		$7.62 \pm .28$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
(b) Considered as zero time for rate calculations.
% Sulfone at infinity: 20.0.

TABLE LXXIII

RATE OF REACTION OF 2-PHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02166 M) IN ANHYDROUS ACETIC ACID AT 25.0° WITH ADDED SODIUM
ACETATE (.05600 M) AND TETRABUTYLAMMONIUM BROMIDE (.06682 M).
RUN II-55.

Aliquot: 4.983 ml.

Time (sec.)	$\log \frac{I_0}{I} (a)$	$10^6 k, \text{ sec.}^{-1}$
0	0.03463	
7,200	.05614	(5.09)
14,400	.09587	7.47
27,000	.13450	6.73
39,600	.17811	6.89
57,600	.23223	6.92
90,900	.33143	7.49
107,400	.35353	7.05
172,800	.44576	6.67
218,700	.49360	6.60
253,800	.54407	7.42
504 hrs.	.63548	
552 hrs.		

Average: $7.03 \pm .29$

(a) Absorbance at 1308 cm.^{-1} in CCl_4 .
% Sulfone at infinity: 19.4.

TABLE LXXIV

RATE OF REACTION OF 2-*p*-BROMOPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02079 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.04507 M), RUN II-229,230.

Base: NaOCH₃ (.03888 M),

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.697 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I}$ (a)	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.040			
0	.051	0.00000		
1,800	.357	.03302	7.43	6.60
3,900	.672	.06558	7.51	6.46
6,300	.996	.10037	7.75	6.61
9,000	1.304	.12840	7.98	6.36
12,600	1.582	.16732	7.80	6.66
18,000	1.913	.20686	7.96	6.71
108,000	2.515	.29469		
223,200	2.479			

Average: 7.74 \pm .18 6.57 \pm .10

(a) Absorbance at 1310 cm.⁻¹ in CCl₄.

% Infinity titer: 90.7.

% Sulfone at infinity: 10.0.

TABLE LXXV

RATE OF REACTION OF 2-p-BROMOPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFI-
NATE (.02091 M) IN 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE(.04762M)
RUN II-243,244.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.713 ml.

Time (sec.)	Titer (ml.)	Corrected Titer(ml.)(a)	$\log \frac{I_0}{I} (b)$	$10^5 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.091				
0	.175	0.175	0.00000		
1,800	.388	.388	.03100	4.79	(4.02)
3,600	.604	.604	.07041	5.05	4.80
6,300	.902	.902	.11160	5.26	4.60
9,900	1.257-.030=1.227		.17114	5.26	4.92
12,600	1.445-.050=1.395		.20898	5.08	5.05
16,500	1.709-.055=1.654		.25406	5.16	5.15
19,800	1.865-.065=1.800		.26811	5.01	4.68
26,100	2.154-.077=2.077		.33626	5.11	5.43
144,600	3.066-.331=2.748				
144,600	3.079-.331=2.759		.44389		
273,600	3.048-.352=2.696				
322,200	3.119-.388=2.731				

Average: 5.09 \pm .11 4.95 \pm .23

(a) Corrections subtracted, based on Run II-242.

(b) Absorbance at 1310 cm.⁻¹ in CCl₄.

% Infinity titer: 98.0. % Sulfone at infinity: 14.7.

TABLE LXXVI

CONTROL ON THE STABILITY OF 2,6-DIMETHYLBENZENESULFINIC ACID (.01528 M)
IN 80% DIOXANE AT 90.0° WITH ADDED 2,6-LUTIDINE (.04717 M), RUN II-242.

Base: NaOCH_3 (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated initial titer: 1.982 ml.

Time (sec.)	Titer (ml.)	Time (sec.)	Titer (ml.)
0	2.105	16,500	2.152
1,800	2.112	19,800	2.162
3,600	2.110	26,100	2.174
6,300	2.105	153,000	2.420
9,900	2.127	273,600	2.469
12,600	2.147	322,200	2.505

TABLE LXXVII

RATE OF REACTION OF 2-p-TOLYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02131 M) IN ANHYDROUS ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE
(.04417 M). RUN II-167,168.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.765 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I}{I^0} (a)$	$10^4 k, \text{ sec.}^{-1}$ titr.	i. r.
Blank	0.429			
0	.567			
120(b)	.783	0.11594	10.06	
270	1.014	.15927	9.94	9.71
300	1.072	.16791	10.31	9.87
600	1.395	.23274	9.55	9.48
750	1.538	.25840	9.55	9.37
960	1.712	.29994	9.62	10.21
1,080	1.800	.30771	9.72	9.55
1,380	1.965	.34044	9.66	9.96
1,710	2.134	.37347	10.20	10.31
8,400	2.465			
18,000	2.466	.43553		
25,200	2.467			
			Average:	9.85 \pm .25 9.81 \pm .28

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

(b) Considered as zero time for infrared rate calculations.

% Infinity titer: 89.2. % Sulfone at infinity: 13.0.

TABLE LXXVIII

RATE OF REACTION OF 2-*p*-TOLYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02288 M) IN ANHYDROUS ETHANOL AT 70.0° WITH ADDED 2,6-LUTIDINE
(.04464 M) AND TETRABUTYLAMMONIUM 2,6-DIMETHYLBENZENESULFINATE
(.05617 M). RUN III-23.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: *p*-Naphtholbenzein.

Calculated infinity: 2.968 ml.

Time (sec.)	Titer (ml.)	10 ⁴ k, sec. ⁻¹
Blank	0.027	
0	.113	
0	.116	
30	.198	(11.50)
120	.336	9.43
150	.458	10.10
240	.615	9.56
345	.806	9.65
450	.982	9.76
660	1.296	10.03
900	1.549	9.84
1,200	1.809	9.88
18,000	2.542	
18,000	2.568	
Average:		9.78 ±.18

% Infinity titer: 85.6.

TABLE LXXIX

RATE OF REACTION OF 2-p-TOLYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.02144 M) IN 80% DIOXANE AT 70.0° WITH ADDED 2,6-LUTIDINE (.04568 M)
RUN II-175,176.

Base: NaOCH₃ (.03888 M)

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.782 ml.

Time (sec.)	Titer (ml.)	$\log \frac{I_0}{I} (a)$	$10^4 k, \text{ sec.}^{-1}$ titr.	i.r.
Blank	0.482			
0	.659	0.07041		
330	.995	.19340	6.82	6.97
480	1.128	.24846	6.88	7.35
660	1.260	.27554	6.77	6.70
960	1.482	.37511	7.09	7.41
1,320	1.702	.44012	7.44	7.28
1,560	1.796	.48302	7.34	7.49
1,800	1.872	.51121	7.22	7.40
2,160	1.956	.53857	6.96	7.04
2,520	2.030		6.85	
2,880	2.105		7.00	
3,300	2.172	.60531	7.20	6.78
4,200	2.234	.64503	6.87	7.63
21,600	2.331			
30,600	2.322	.66932		
43,200	2.329			

Average: 7.04 \pm .19 7.21 \pm .27

(a) Absorbance at 1308 cm.⁻¹ in CCl₄.

% Infinity titer: 83.6.

% Sulfone at infinity: 20.0.

TABLE LXXX

RATE OF REACTION OF 2-p-NITROPHENYL-2-PROPYL 2,6-DIMETHYLBENZENE-SULFINATE (.02143 M) IN ANHYDROUS ACETIC ACID AT 90.0° WITH ADDED SODIUM ACETATE (.05600 M). RUN II-253.

Internal standard: Ethylene carbonate.

Time (sec.)	Ester Concentration(a)	$\log \frac{A}{A_0}$	$10^6 k, \text{sec.}^{-1}$
0	3.014		
25,200	2.452	0.08962	8.19
50,400	2.019	.17400	7.95
79,200	1.673	.25564	7.43
133,200	1.134	.42453	7.34
172,800	.792	.58041	7.74
			Average: $7.73 \pm .28$

(a) Area ratio of n.m.r. peak at 7.40 τ to ethylene carbonate peak at 5.48 τ as measured in CHCl_3 .

TABLE LXXXI

RATE OF REACTION OF 2-p-NITROPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE
(.01100 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.01716 M)
RUN III-25.

Base: NaOCH₃ (.03888 M).

Aliquot: 25.00 ml.

Indicator: Phenolphthalein.

Theoretical infinity: 7.09 ml.

Time (hrs.)	Titer (ml.)	10 ⁶ k, sec. ⁻¹
0	0.108	
28	0.66	1.15
72	1.017	0.77
115	1.447	0.74
139	3.570	2.30
188	3.738	1.86
259	4.072	1.63
Infinity ^(a)	5.170	

Average: 1.41₋.51

(a) Infinity point calculated on the basis of 73% solvolysis and the formation of 27% ethyl 2,6-dimethylbenzenesulfinate, as found in Run III-26,27 (Table LXXXII).

TABLE LXXXII

RATE OF REACTION OF 2-p-NITROPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.01100 M) IN ANHYDROUS ETHANOL AT 90.0° WITH ADDED 2,6-LUTIDINE (.01716 M). RUN III-26, 27.

Internal standard: Ethylene carbonate. Aliquot: 25.00 ml.

Time (hrs.)	<u>p</u> -nitro Ester conc. (a)	F* (b)	Ethyl Ester conc. (c)	(d) $10^6 k, \text{sec.}^{-1}$	(e)
0	2.200	0	0		
28	1.975	0.51		1.08	
72	1.710	.92		.97	
115	1.430	.27	0.208	1.03	1.04
139	.891	.22	.278	(1.80)	1.26
188	.800	.28	.394	1.47	1.63
259	.525	.29	.487	1.55	1.84

Average: $1.21 \pm .23$ $1.44 \pm .29$

$$k_{\text{obs. avg.}} = 1.32 \times 10^{-6} \text{ sec.}^{-1}$$

$$k_{\text{solv.}} = k_{\text{obs.}} (1 - F^*) = 9.5 \times 10^{-7} \text{ sec.}^{-1}$$

$$k_{\text{ethyl ester}} = k_{\text{obs.}} F^* = 3.5 \times 10^{-7} \text{ sec.}^{-1}$$

- (a) Area ratio of n.m.r. peak at 7.40 τ to ethylene carbonate peak at 5.48 τ (chloroform) at 100 Mc.
 (b) Ratio of ethyl 2,6-dimethylbenzenesulfinate formed to 2-p-nitrophenyl-2-propyl 2,6-dimethylbenzenesulfinate reacted as measured by n.m.r. peaks at 7.32 and 7.40 τ .
 (c) Area ratio of n.m.r. peak at 7.32 τ to ethylene carbonate peak at 5.48 τ (chloroform) at 100 Mc.
 (d) Rate constant for arenesulfinate ester disappearance following peak at 7.40 τ .
 (e) Rate constant for arenesulfinate ester disappearance following peak at 7.32 τ .

TABLE LXXXIII

RATE OF REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENE-SULFINATE (.02153 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE (.04349 M). RUN II-250.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: Phenolphthalein.

Calculated infinity: 2.794 ml.

Time (sec.)	Titer (ml.)	10 ³ k, sec. ⁻¹
0	1.365	
60	1.406	0.76
135	1.551	1.63
190	1.766	2.92
310	1.779	1.87
460	2.067	2.96
670	2.058	1.98
5,040	2.310	
5,040	2.304	

Average: 2.0 ± .6

% Infinity titer: 83.0.

TABLE LXXXIV

RATE OF REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFI-
NATE (.02334 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE
(.04495 M). RUN II-262.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: p-Naphtholbenzein.

Calculated infinity: 3.028 ml.

Time (sec.)	Titer (ml.)	$10^3 k, \text{sec.}^{-1}$
0	0.344	
65	.618	2.13
125	.830	2.09
200	1.053	2.04
285	1.275	2.01
385	1.465	1.96
560	1.769	1.98
3,420	2.461	
5,520	2.465	
Average: $2.04 \pm .05$		

% Infinity titer: 81.3.

TABLE LXXXV

RATE OF REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFI-
NATE (.01968 M) IN ANHYDROUS ETHANOL AT 0.0° WITH ADDED 2,6-LUTIDINE
(.04358 M). RUN II-278.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: p-Naphtholbenzein.

Calculated infinity: 2.554 ml.

Time (sec.)	Titer (ml.)	10 ⁴ k, sec. ⁻¹
0	0.168	
410	.245	1.01
1,800	.504	1.08
3,000	.688	1.06
5,400	.976	1.02
9,480	1.341	1.01
14,400	1.666	1.07
87,180	2.075	
140,100	2.069	

Average: 1.04 ± .03

% Infinity titer: 81.1.

TABLE LXXXVI

RATE OF REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02257 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE (.04554 M) AND TETRABUTYLAMMONIUM 2,6-DIMETHYLBENZENESULFINATE(.03346 M).
RUN III-34.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: p-Naphtholbenzein.

Calculated infinity: 2.928 ml.

Time (sec.)	Titer (ml.)	10 ³ k, sec. ⁻¹
0	0.567	
40	.709	2.05
90	.862	1.99
170	1.092	2.03
300	1.390	2.03
435	1.615	2.00
660	1.908	2.07
3,360	2.361	
6,660	2.377	

Average: 2.03 ± .02

% Infinity titer: 80.9.

TABLE LXXXVII

RATE OF REACTION OF 2-*p*-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFONATE (.02217 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE (.04662 M) AND LITHIUM PERCHLORATE (.03690 M). RUN II-261.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: *p*-Naphtholbenzein.

Calculated infinity: 2.877 ml.

Time (sec.)	Titer (ml.)	10 ³ k, sec. ⁻¹
0	0.870	
55	.999	2.45
140	1.325	2.58
205	1.462	2.56
280	1.619	2.57
365	1.753	2.52
550	1.965	2.47
3,925	2.346	
5,245	2.354	
		Average: 2.53 ± .05

% Infinity titer: 81.7.

TABLE LXXXVIII

RATE OF REACTION OF 2-*p*-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFINATE (.02222 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE (.04670 M) AND TETRABUTYLAMMONIUM 4-METHYLBENZENESULFINATE (.25938 M).
RUN II-279.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: *p*-Naphtholbenzein.

Time (sec.)	Titer (ml.)	10 ³ k, sec. ⁻¹
0	2.660	
70	2.839	1.99
115	2.965	2.18
220	3.135	1.92
265	3.210	1.92
375	3.337	1.80
540	3.559	1.96
2,680	4.029	
5,760	4.046	

Average: 1.96_±.09

TABLE LXXXIX

RATE OF REACTION OF 2-p-METHOXYPHENYL-2-PROPYL 2,6-DIMETHYLBENZENESULFI-
NATE (.02323 M) IN ANHYDROUS ETHANOL AT 25.0° WITH ADDED 2,6-LUTIDINE
(.04463 M) AND TETRABUTYLAMMONIUM AZIDE (.029130 M). RUN III-35.

Base: NaOCH₃ (.03888 M).

Aliquot: 5.046 ml.

Indicator: p-Naphtholbenzein.

Calculated infinity: 3.013 ml.

Time (sec.)	Titer (ml.)	10 ³ k, sec. ⁻¹
0	0.235	
45	.315	1.99
105	.417	2.07
185	.525	2.01
300	.670	2.10
450	.791	2.01
670	.951	2.18
2,700	1.171	
5,580	1.165	
		Average: 2.06 ± .06

% Infinity titer: 38.8.

BIBLIOGRAPHY

1. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N.Y. (1953), p. 388.
2. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Co. Inc., New York (1940), p. 171.
3. W. G. Young, S. Winstein and H. L. Goering, J. Am. Chem. Soc., 73, 1958 (1951).
4. S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, ibid., 78, 328 (1956).
5. S. Winstein and G. C. Robinson, ibid., 80, 169 (1958).
6. S. Winstein P. E. Klinedienst Jr. and G. C. Robinson, ibid., 83, 885 (1961).
7. H. L. Goering, M. M. Pombo and K. D. McMichael, ibid., 85, 965 (1963).
8. S. Winstein, A. Ledewith and M. Hojo, Tetrahedron Letters No. 10, 341 (1961).
9. Y. Pocker, Proc. Chem. Soc., 140 (1961).
10. H. L. Goering and J. F. Levy, Tetrahedron Letters No. 18, 644 (1961).
11. H. L. Goering, R. G. Briody and J. F. Levy, J. Am. Chem. Soc., 85, 3059 (1963).
12. H. L. Goering and J. F. Levy, ibid., 86, 120 (1964).
13. S. G. Smith, Tetrahedron Letters, No. 21, 979 (1962).
14. A. Iliceto, A. Fava, O. Mezzucato and O. Rossetto, J. Am. Chem. Soc., 83, 2729 (1961).
15. D. Darwish, Unpublished results.
16. J. Noreyko, M. Sc. Thesis, University of Alberta (1963).
17. J. Kenyon and H. Phillips, J. Chem. Soc., 1676 (1930).
18. J. Kenyon, H. Phillips and F. M. H. Taylor, ibid., 173 (1933).
19. J. Kenyon, H. Phillips and G. R. Shutt, ibid., 1663 (1935).

20. C. L. Arcus, M. P. Balfe and J. Kenyon, ibid., 485 (1938).
21. A. Streitwieser Jr., Solvolytic Displacement Reactions, McGraw-Hill Book Co. Inc., New York (1962), p. 92.
22. A. C. Cope, D. E. Morrison and L. Field, J. Am. Chem. Soc., 72, 59 (1950).
23. A. H. Wragg, J. S. McFadyen and T. S. Stevens, J. Chem. Soc., 3603 (1958).
24. R. A. McLaren, Ph. D. Thesis, University of Alberta (1964).
25. D. Darwish and E. A. Preston, Tetrahedron Letters, No. 2, 113 (1964).
26. H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 79, 1913 (1957).
27. M. E. Hanke, ibid., 45, 1325 (1923).
28. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen & Co., Ltd., London (1958), p. 360.
29. V. N. Ipatieff, H. Pines and B. S. Friedman, J. Am. Chem. Soc., 60, 2731 (1938).
30. D. S. Tarbell and D. K. Fukushima, Organic Syntheses, John Wiley & Sons. Inc., New York (1955), Collected Volume III, p. 809.
31. M. P. Balfe and J. Kenyon, J. Chem. Soc., 3309 (1950).
32. A. G. Davies, R. V. Forster and R. Nery, ibid., 2204 (1954).
33. Reference 28, p. 34.
34. E. S. Wallis and P. I. Bowman, J. Org. Chem., 1, 383 (1937).
35. Reference 28, p. 273.
36. A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2763 (1956).
37. A. H. Fainberg and S. Winstein, ibid., 79, 1602 (1957).
38. Reference 21, p. 42.
39. H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, J. Am. Chem. Soc., 79, 1897 (1957).
40. M. C. Church, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 966 (1940).

41. M. S. Silver, J. Am. Chem. Soc., 83, 404 (1961).
42. M. C. Caserio, D. L. Glusker and J. D. Roberts, ibid., 81, 336 (1959).
43. J. L. Kice and K. B. Bowers, ibid., 84, 605 (1962).
44. C. A. Bunton and B. N. Hendry, J. Chem. Soc., 627 (1963).
45. S. G. Smith, A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 83, 618 (1961).
46. D. Darwish and R. A. McLaren, Tetrahedron Letters, No. 26. 1231 (1962).
47. S. Winstein, J. S. Gall, M. Hojo and S. Smith, J. Am. Chem. Soc., 82, 1010 (1960).
48. S. Winstein, A. H. Fainberg and E. Grunwald, ibid., 79, 4146 (1957).
49. W. T. Miller Jr. and J. Bernstein, ibid., 70, 3600 (1948).
50. A. H. Fainberg and S. Winstein, ibid., 79, 1597 (1957).
51. A. H. Fainberg and S. Winstein, ibid., 78, 2770 (1956).
52. A. Klages, Ber., 35, 2637 (1902).
53. H. C. Brown, Y. Okamoto and G. Ham, J. Am. Chem. Soc., 79, 1906 (1957).
54. S. Choe and S. Tsutsumi, Nippon Kagaku Zasshi, 81, 582 (1960), see also C. A. 56, 397^d.
55. H. Kwart and P. S. Francis, J. Am. Chem. Soc., 77, 4907 (1955).
56. I. Heilbron and H. M. Bunbury, A Dictionary of Organic Compounds Eyre & Spottiswoode, London (1953), Volume IV p. 155.
57. Reference 56, Volume III p. 507.
58. M. S. Malinowskii and A.A. Yavorovskii, Ukrain. Khim. Zhur., 21, 240 (1955), see also C. A. 50, 9313^b.
59. K. Ziegler and P. Tieman, Ber., 55, 3406 (1922).
60. E. Bergman and A. Weizmann, Trans. Faraday Soc., 32, 1327 (1936).
61. A. W. Weitkamp, Flavor Reserach and Food Acceptance, 331 (1958), see also C. A. 53, 10276^c.
62. D. Seymour and K. B. Wolfstirn, J. Am. Chem. Soc., 70, 1177 (1948).

63. S. Braverman, Ph. D. Thesis, University of Alberta (1963).
64. H. Lund and J. Bjerrum, Ber., 64, 210 (1931).
65. L. F. Fieser, Experiments in Organic Chemistry, Third Edition, D. Heath & Co., Boston (1957), p. 284.
66. H. C. Brown, S. Johnson and H. Podall, J. Am. Chem. Soc., 76, 5556 (1954).
67. S. Winstein and R. Adams, ibid., 70, 840 (1948).
68. S. Winstein, P. E. Klinedienst Jr. and E. Clippinger, ibid., 83, 4986 (1961).
69. P. M. Nair and J. D. Roberts, ibid., 79, 4566 (1957).
70. J. A. Pople, Mol. Phys., 1, 3 (1958).
71. J. S. Waugh and F. A. Cotton, J. Phys. Chem., 65, 562, (1961).
72. M. Oki and H. Iwamura, Bull. Chem. Soc. Japan, 35, 1428 (1962).
73. L. M. Jackman, Applications of Nuclear Magnetic Resonance in Organic Chemistry, Pergamon Press, New York (1959), p. 101.
74. E. Tommila and C. N. Hinshelwood, J. Chem. Soc., 1801 (1938).
75. Reference 2, p. 184.
76. R. W. Taft Jr., J. Am. Chem. Soc., 79, 1045 (1957).
77. P. B. D. de la Mare, J. Chem. Soc., 3823, (1960).
78. H. van Bekkum, P. E. Verkade and B. M. Wepster, Rec. trav. chim., 78, 815 (1959).
79. S. Winstein and E. C. Friedrich and S. Smith, J. Am. Chem. Soc., 86, 305 (1964).



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